STUDIES ON THE COMPLEXES
OF
TRANSITION METALS WITH AMINO ACIDS
AND
HETEROCYCLIC AMINES

THESIS
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A B S T R A C T

Studies on the complexes of chromium(II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(VI) sulphate with some aminoacids.

The complexes of chromium (II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(VI) sulphate with various aminoacids such as glycine, L-asparagine, DL-valine, DL-serine, DL-leucine, L-leucine, L-proline, DL-α-alanine and β-alanine have been studied in solution. With chromium(II) chloride, the interaction with sulphur containing aminoacids such as cysteine, methionine and taurine has also been studied. The studies are mainly concerned with the composition and stability of metal aminoacid complexes formed in solution by employing electrometric techniques of potentiometry and conductometry.

A combining ratio of 1:1 for the metal and aminoacid was obtained in each of the complexes as is evident from the results, of electrometric titrations. The stability constants of the aminoacid complexes were determined by performing pH-metric titrations with the mixtures containing (a) aminoacid, (b) metal and (c) aminoacid + metal, using standard KOH as a titrant. The value of formation constant was evaluated by applying Bjerrum's method, simplified by Albert for aminoacid system.

The observed and the calculated values of the stability constants for the various metal aminoacid complexes are given in table 36, chapter I. It appears that the observed values were in good agreement with those calculated from the equations IV, V, VI, VII and IX, chapter I.

For β-alanine, DL-α-alanine and L-proline complexes, the order of stability is: $UO_2^{2+} \approx Cr^{2+} > Ti^{3+} > VO^{2+}$. In case of L-esparagine and DL-serine complexes, the metals follow the order: $Ti^{3+} > Cr^{2+} \approx VO^{2+} > UO_2^{2+}$. The order of stability of L-leucine and DL-valine complexes is: $VO^{2+} \approx Cr^{2+} > UO_2^{2+} > Ti^{3+}$. In general, the order of stability constants in metal complexes is: L-proline > β-alanine > DL-α-alanine >glycine > L-leucine > DL-valine > DL-serine > L-asparagine, which with a few exceptions is the same as that of increasing pK_a order of aminoacids.

The Cr^{2+} complexes with sulphur containing aminoacids follow the stability order: cysteine > methionine > taurine. On the basis of the comparison of log K' and log K_s values for cysteine and those for glycine, and DL-α-alanine complexes, the coordination through COO^-, NH_2 and -S- has been suggested. The bonding through NH_2 and COO^- in methionine complexes has been inferred on the basis of similar comparative study.

Behaviour of copper(I) iodide in aqueous potassium iodide containing aminoacids:

The possibility of complex formation between copper(I) and aminoacids has been investigated on the basis of the characteristic of copper(I) halide to become soluble in aqueous alkali halide solution. Evidence for the complex formation between copper(I) iodide and aminoacid such as L-leucine, L-proline and glycine has been obtained from the results of solubility data. The copper contents in two sets of solutions, the one without and the other with aminoacid differ considerably (table 2A, 2B and 2C, chapter II). The concentration of aminoacid consumed in complex formation was calculated by the difference of the concentration of aminoacid added initially to that estimated from the cuprous solutions, colorimetrically. From the solubility data, there is an indication of 1:1 complex formation with L-leucine and L-proline, and 1:2 complex species in case of glycine. The results are further substentiated from the slopes of the plots between free aminoacid concentration [L] and the solubility product of the aminoacid complex, Ksp (Fig.2, chapter II).

Substitution reactions of tetrakis (thiourea) palladium(II) chloride with some aminoacids:

The kinetics of the substitution reactions of square planar complex, $Pd(tu)_4Cl_2$ with some aminoacids such as

glycine, DL-α-alanine, threonine, L-asparagine, DL-valine, DL-serine and L-proline has been studied, spectrophotometrically. The first order rate constant, $K_{obsd.}$ was evaluated from the slope of the linear plots between time, t and log $\frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$ (Fig. 1 to 7, chapter III).

Linear plots were also obtained by plotting K_{obsd} and [Y], the concentration of aminoacid (Fig. 8 , chapter III). These results indicate that the substitution reaction proceed by a displacement mechanism following the famous two term rate law, suggested by Basolo. The rates of K_1 and K_2, the first and second order rate constant, respectively, were determined from the intercept and slope of the linear plot. The values of K_{obsd}, K_1 and K_2 are given in table No.8, chapter III. The rate constant K_1 represents the slow displacement of thiourea molecules by the solvent, H_2O which is then readily displaced by the aminoacids. However, the second order constant, K_2 is responsible for the direct nucleophilic displacement by the aminoacid.

Transition metal complexes of the alkaloids:

The interaction of alkaloids such as quinaldine, quinine, brucine and codeine with transition metal ions results in the formation of stable complexes. In general, the complexes are highly soluble in water and insoluble in alcohol.

acetone, ether, chloroform etc. With quinaldine and codeine, there is formation of 1:2 complexes whereas with quinine and brucine 1:1 complex species are formed. The nature of the coordination in the solid complexes has been investigated on the basis of infra red spectral studies. The site of coordination in the metal - alkaloid complexes was located by comparing the spectra of the complexes with those of the respective alkaloid and studying the major changes or shifts occurred on coordination.

From the studies of the infra red spectra of quinaldine and its complexes with $TiCl_3$, $VOCl_2$ and UO_2SO_4, coordination through heterocyclic nitrogen is suggested. The conclusion is mainly based upon the changes took place in the regions of ring CC, CN stretching, ring skeletal and CH out of plane vibrations. The changes in these regions are depicted by the increase in the wave number and increase in number of bands on coordination. The changes are most marked in the vanadyl and least in the case of titanous chloride complex (table 1, chapter IV).

Out of these possible coordination sites namely, heterocyclic nitrogen of 6-methoxy quinoline, nitrogen of the paraffinic quinuclidine, and secondary OH group present at the junction of two ring systems. The infra red spectra of the

quinine and its complexes with $VOCl_2$, $TiCl_3$ and UO_2SO_4 give considerable evidence of coordination through heterocyclic nitrogen of the substituted quinoline. The evidence is based upon the changes occurred in the regions of ring CC, CN stretching vibrations of 6-methoxy quinoline, ring skeletal vibrations of heterocyclic aromatic ring and CH out of plane deformation vibrations. The bands in these regions are shifted to higher frequency side with increase in the number of the bands. There are no noticeable changes in the positions of the bands arising from the secondary hydroxy stretching vibrations and CN stretching vibrations of quinuclidine ring (table 2, chapter IV).

There are three pertinent sites for coordination in the brucine namely, -NCO (acylazole group), the oxygen of the 7-membered oxepine ring and the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring. Sufficient evidence for the coordination through nitrogen of the acylazole group has been obtained on comparing the spectrum with those of its complexes with $VOCl_2$, $TiCl_3$ and UO_2SO_4. The CO, CN stretching modes of n-acylazole system belonging to keto-piperazine ring system occurred at 1626 and 1335cm^{-1}, respectively. The spectra of the complexes are devoid of these bands. There are no appreciable changes in the positions of the bands arising from

CO stretching of the 7-membered oxepine ring and CN stretching of bridge head tertiary nitrogen of the 5/6 pyrrocoline ring. This excludes the possibilities of coordination through these sites(table 3, chapter IV).

The infra red spectra of codeine and its complexes with Cu^{2+}, CO^{2+}, Ni^{2+}, VO^{2+}, Mn^{2+}, Cr^{3+} and Ti^{3+} give some important clues regarding the bonding in these complexes. The alkaloid, codeine has three sites susceptible to coordination [illegible] namely, the secondary hydroxy group, tertiary nitrogen attached to methyl group and oxygen of the furan ring. The fact that secondary OH stretching vibrations occurring at $3600cm^{-1}$ in the codeine, do not appear in the complexes at this frequency or near by regions, is a conclusive evidence for coordination through secondary OH group in metal - codeine complexes. The possibilities of coordination through CH_3-N or oxygen of the dihydrofuran ring are quite remote. No appreciable shifts are noted in the CH_3-N stretching, and CC, CO ring stretching, CH in and out of plane, and ring skeletal vibrations of dihydrofuran ring (table 4, chapter IV).

This is to certify that the work described in the thesis entitled" Studies on the complexes of transition metals with aminoacids and heterocyclic amines" is an original contribution of Mr. Omar Farooq and is suitable for submission for the degree of Ph.D.

Anees U Malik

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23-12-10

A_C_K_N_O_W_L_E_D_G_E_M_E_N_T

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Omar Farooq

(OMAR FAROOQ)

TO

PARENTS

LIST OF PUBLICATIONS

1. "Studies on the complexes of chromium(II) chloride with some aminoacids". J.Electroanal.Chem.,24, 233(1970).

2. "Composition and stability of uranyl, vanadyl and titanous complexes with some aminoacids", J.Electroanal.Chem., 24, 464 (1970).

3. "Complexes of chromium(II) chloride with some sulphur containing aminoacids" J.Electroanal. Chem., 26, 411 (1970).

C O N T E N T S

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GENERAL INTRODUCTION

The field of coordination chemistry, first initiated by Alfred Werner[1] in the last decade of the nineteenth century, is one of the most promising chapters in the realm of chemistry. There are several factors which contributed to its emergence as the most versatile field in the domain of inorganic chemistry. The coordination compounds have played an important role in the progress of chemistry in the sense that every theory relating to the structure of inorganic compounds and chemical bonding has chosen coordination complexes as a testing ground. With the application of quantum mechanics to the theories of chemical bonding, the theoretical approach to the area of coordination chemistry becomes more quantitative and less logical involving some basic principles of physics and mathematics. Some modern coordination theories, such as the molecular orbital[2] and ligand field[3] theories are the results of the combined efforts made by the assembly of scientists including physicists and mathematicians.

The applications of coordination compounds are well known. They are extensively used in industry e.g., metallurgical processes, electroplating, water softening, higher polymer syntheses etc. In analytical chemistry, the use of complexes in the qualitative and quantitative determinations of organic and inorganic substances, and ions is inevitable.

The part played by the coordination compounds in biological processes is no less fascinating. The chlorophyll, hemoglobin and vitamin B_{12} are some of the very common examples of naturally existing coordination compounds. Some of the vital life processes directly or indirectly are dependent on the function of coordination compounds.

Amongst a large number of natural products belonging to the biological systems, the proteins, aminoacids and prophyrins are found to form an efficient group of ligands having high affinity towards metal cations and this is because of the presence of some powerful coordinating groups present in these compounds and possession of some specific properties missing in other natural products.

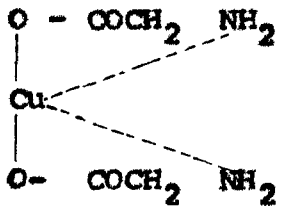
Aminoacids are water soluble, amphoteric electrolytes and having ability to form acidic and basic salts and thus acting as buffers over at least two ranges of pH due to the presence of amino and carboxylic groups. They are dipolar ions with high electric moments with the capacity to increase the dielectric constant of the solvent in which they are dissolved. The presence of reactive groups enables them to participate in a variety of chemical transformations and degradations forming products such as esters, amides, amines, polymers polypeptides, hydroxy acids, ketoacids, short or long chain acids, all of which are directly or

indirectly connected with the biological processes. Amino-acids are indispensable constituents of the diet of all living beings including man and participants in crucial metabolic reactions on which life depends and substrates for a variety of specific enzymes in vitro. Almost all the naturally occurring aminoacids belong to α-category with asymmetric centres essential constituents of protein molecules. The latter are characterised biologically and chemically by the number, distribution and spatial inter-relation of aminoacids from which they are derived[4].

The similarities in naturally occurring aminoacids exist in the respect that they possess optical rotation at the α-carbon atom. But dissimilarities exist in the sense that each possesses a different side chain which distinguishes them individually from the others chemically and biologi-cally.

The chemical reactivity of aminoacids as potential coordinating ligands lies in the presence of two effective donor atoms in the common skeleton NH_2-CHR-COO^-, each of the natural aminoacid is thus capable of forming a stable 5-membered chelate ring. Some of the aminoacids may contain effective donor atoms in the chain R and have the capability to complete with α-amino and carboxylic groups.

The first systematic study of metal-aminoacid interaction was carried out by Ley[5,6] in early part of the twentieth century when he investigated the reaction of glycine with copper salts. Ley reported[7] that diglycinate copper(II) salts, were, unlike sodium and potassium salts of glycine, highly nonconducting and he attributed it to the formation of "inner complex salts" with the following structure.



Ley's formulation was based upon the similarities between aminoacid and ammonia complexes both exhibiting blue colour in aqueous solutions and the green colour of the solutions of phenyl glycine complex, and the corresponding aniline complex. Further Ley[6] and others[8,9] showed that although α and β-aminoacids form stable complexes with copper (II), υ and δ-aminoacids did not. The stability of the Ni(II) and Cu(II) complexes diminished in the following order:[6,8,9] Glycine > α-alanine > β-alanine > (γ, δ, and ε-aminoacids). From the above formulations it appears that the stability of Cu(II) and Ni(II) complexes decreases with increase in side

chain length and the distance between amino and carboxylic groups. However, the latter conclusion was found to be incorrect as indicated by the work of Abderhaldein and Schnitzer,[10] and Birkofer and Hartwig.[11] They presented evidence of increasing stability with increased length of the side chain. However, it is now believed that stability in general, is independent of the nature of the side chain but dependent of dissociation constant of the complexing nitrogen. The fact that the stability of 5-membered ring plays main role in aminoacid complexes is demonstrated by the formation of most stable complexes with α-aminoacids, whereas β-aminoacids complexes being less stable form 6-membered ring. The γ-, δ- and ε-aminoacids will form complexes involving more than 6-membered rings and will be thus unstable.[12] Another factor effecting the stability of the metal-aminoacid system is the coordinating ability of the metal. Thus chromium(VII) being relatively poor electron acceptor form stable complexes with glycine but fails to show any reactivity with β-alanine.[13] One more interesting aspect of the coordination chemistry of aminoacid complexes is the combination of the ligand in more than one way in the same complex. Green and Ang[14] have reported that certain Cr(III) complexes of DL-alanine may contain alanine partially in chelate combination and partially in coordination through carboxylate group alone.

Amongst the sulphur containing aminoacids, the complexes with cysteine have been widely studied. The interaction of divalent metals e.g., Fe^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+} etc., with cysteine has been reported by a number of workers. As early as in 1929 Michaelis and Barron[15] observed that, when cysteine was treated at pH 7.3 to 8.5, a green colour was produced uneffected by the presence or absence of oxygen. However, the reaction with Co^{2+} was found to be air sensitive and the brown colour which developed as a result of oxidation being at a maximum when the initial ratio of cysteine and cobalt was 3:1, no cystine seemed to be formed as a result of the oxidation.[16] Under identical conditions the oxidation of Fe^{2+}-cysteine complex led to a violet colour with the production of cystine.[17] The iron complex is much more labile than the cobalt complex, permitting the former metal to serve as a catalyst. The ready oxidation of cysteine into cystine greatly complicates the study of metal complexes. For example, cysteine is readily oxidised by Cu^{2+} amonical solutions.[18] If excess of cysteine is present it reacts with Cu(I) to form a stable complex, whose log K_1 has been found to be 19.19 at 25°C. The overall reaction with Cu^{2+} may be written, $4RS^- + 2Cu^{2+} \rightleftharpoons 2RSCu + RSSR$. Other metal ions that can undergo changes in the valency such as Fe and Mn also act as a catalyst for the autoxidation.[19] While studying Co^{2+} complexes Albert[20] concluded that the

sulphydryl and amino groups of the cysteine were bound to Co^{2+}. With Pb^{2+}, cysteine is believed to act as a tridentate ligand.[21] Other sulphur containing aminoacids such as methionine and taurine combine with Cu^{2+}, Co^{2+} and Fe^{2+} to an extent typical of monoamino monocarboxylic acids.[22] Methyl-2-amino-ethyl sulphide, $CH_3\ SCH_2\ CH_2\ (NH_2)\ COOH$ reacts with Ni(II) and Cu(II)[23] much less strongly than ethylenediamine or methionine. This indicates that thioether contributes little to the stability of the metal complexes. It was concluded, therefore, that sulphur containing amine was involved in linkage because 3 mols. of ligand reacted with Ni(II) and two mols. with Cu(II) to give hexa and tetra coordinate species, respectively. From the studies of Pfeiffer,[24,25] it appears that due to the splitting of the thioether bond in the cytochrome, there is some possibility that thioether linkage in methionine may be attacked by Pb(II), Cu(II) and Cd(II) in addition to Ag(I) and Hg(II). There is little doubt, however, that in methionine the carboxyl and amino-groups are normally responsible for chelation with the metal ions which have been studied uptill now.

The recent literature on metal aminoacid complexes is abounded with numerous references concerning various aspects of this field. The main domain of these studies concerns with the stability and structure of aminoacid complexes specially with transition metals and more specifically with Ni(II),

Cr(III), Co(II) and Cu(II) ions. The studies related to the stability are largely covered by potentiometric, pH-metric and polarographic methods, and the structural studies involve infrared spectral and X-rays investigations.

The earlier investigations on metal-aminoacid complexes, based upon potentiometric and pH-metric titration methods, were carried out by Albert[20,22] who used Bjerrum's method for the determination of stability constants. He determined the stability constants as log K_s of the complexes of divalent aminoacids with metals. The strongest complexes are those of proline and the weakest are those which involve serine, methionine, phenyl alanine and β-alanine. The order of stability of complex formation among the metals is: $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$. Monk[26] studied the behaviour of electrolytes in solutions of aminoacids and calculated the dissociation contants of various transition and other metal ions complexes with glycine, glycylglycine, alanine etc., with the help of solubility measurements and pH-metric titrations. He found that metals Pb^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} form MR^{+} and MR_2 species whereas Mn^{2+}, Mg^{2+} and Ca^{2+} gave only MR^{+} species. Perrin[27] calculated the stability constants of Fe(II) complexes with twenty aminoacids by the potentiometric titration method. The constant K_s varies with

proton, acid and dissociation constants of the aminoacids, but to a much smaller extent as compared with the corresponding ferric complexes. Molar electrode potentials for Fe^{3+} - Fe^{2+} aminoacid complexes, computed from these results, show linear relationship with logarithm of the dissociation constants of aminoacids. Tanford et al.[28] carried out an interesting study on the interactions of Co(II) with glycine, alanine, asparagine and arginine employing Bjerrum's method. The difference between the results of arginine and alanine were successfully treated by the Kirkwood-Westheimer theory,[29] on the basis of the electrostatic influence of the positively charged guinidine group of arginine. The data for asparagine could not be explained in this way, and indicated that the structure of the chelating group NH_2-CHR-COO^- in this molecule was abnormal. The authors reported appreciable changes between the association constants for glycine and those for alanine for which there exists no convincing explanation. Very recently Clarke and Martell[30] studied the chelate systems involving the interactions of Ca(II), Co(II), Cu(II), Hg(II), Mg(II), Mn(II), Ni(II) and Zn(II) with arginine, citrulline and ornithine. The formation constants of the chelates containing 1:1 and 1:2 molar ratios of metal ion to monoprotonated ligand are reported at 25°C. The stability order of the metal chelates followed the order: $Cu^{2+} > Hg^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$. The greater stability of the arginine ligand was interpreted on the basis of the electronic

interactions of the ligand with the metal ions.

After potentiometric and pH-metric methods, the polarographic method has been the most versatile technique used[31-34] for studying the metal-aminoacid complexes. A large number of references are available in recent literature regarding the composition and stability of these complexes. Li and Doody[31] studied, polarographically, the Cu(II) complexes of glutamic acid, phenylalanine, serine, arginine and lysine. The stability of the complexes decreases in the order given. The ratio of aminoacid to copper in each case is 2 to 1 and this ratio is in agreement with the potentiometric data. The results were explained on the basis of the molecular structures of aminoacids. Doody et al.[32] also studied the Cu(II) and Zn(II) complexes with proline, β-alanine, norleucine, methionine and glycylglycine. The formation constants of Cu(II) complexes were determined polarographically having the values 16.63, 12.89, 15.20, 14.75 and 16.65 in the order given above. The composition of 1:2 Zn-aminoacid complex was determined with the help of potentiometry, spectrophotometry and conductometry also.

The isomers of complexes of α-aminoacid with Cu(II) have been reported.[35] The thermodynamic stabilities of three isomers of bisamino-acid Cu(II) i.e., [Cu(D)(L)] and $[Cu(D)_2]$

are shown to be equal for ∝-alanine, phenylalanine, valine and proline. The dark blue crystalline isomers bis -[L(+)-∝-alaninato copper (II)] and of its enantimers were isolated, in addition to the usual light blue forms.

Infrared spectra of aminoacids and their complexes have been studied in detail.[43,44] Band assignments have been made for dipolar ions of glycine,[36] ∝-alanine[37] and β-amino-butyric acid.[38] It has been found that the COO^- stretching bands are most sensitive to the effects of coordination and intermolecular interaction. In general, the antisymmetric stretching frequency is much more sensitive to these influences than the symmetric one. The latter view is examplified by the infra-red results on trans square planar complexes e.g., $[Ni(gly)_2]\ 2H_2O$, $[Zn(gly)_2]\ H_2O$[39] and $[Cd(gly)_2]\ H_2O$.[40] Nakamoto[41] examined the effect of coordination and hydrogen bonding in various metal complexes of aminoacids by measuring COO^- stretching frequencies in different physical states. He concluded that for any one physical state, the same frequency order for a series of metals was always found, regardless of the nature of the ligand. Thus antisymmetric frequencies increase, the symmetric frequencies decrease, and the separation between the two frequencies increases in the following series of metals.

$Ni(II) < Zn(II) < Cu(II) < Co(II) < Pd(II) \simeq Pt(II) < Cr(III)$.

Quagliano and Coworkers,[42] while studying infra red spectra of Cu(II), Ni(II) and Zn(II) glycinates, concluded that the M-O bonds in these complexes were essentially ionic because their frequencies were almost the same as those of potassium glycinate and sodium acetate and these metals used s-p hybrid orbitals in forming linear bonds with the nitrogen of the ligands. They further stated that the two oxygens of carboxyl group were symmetrically arranged with respect to various aminoacids.

Alkaloids are complex nitrogen bases of vegetable origin with marked physiological action. Many alkaloids are highly toxic and plant extracts containing them have been valued as poisons for many centuries. The uses of alkaloids are well known. Quinine as a specific drug for malaria, morphine for the relief of pain, cocaine as a local aneesthetic and atropine in eye surgury are well known examples of the medical applications of these nitrogeneous compounds of vegetable origin.

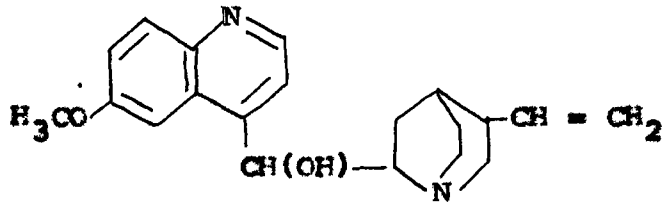
Alkaloids are in general, well crystalline colourless substances, almost insoluble in water but soluble in organic solvents. A majority of the alkaloids are levorotatory but a few of them are dextrorotatory and still fewer optically

inactive. Due to their basic character they have the capability of forming salts with acids which are water soluble.

The alkaloids are composed of four elements viz., carbon, hydrogen, nitrogen and oxygen, nitrogen atom usually forming an integral part of a cyclic structure. Chemically, many of them are closely related and have a common nucleus belonging to pyridine, pyrrole, tropane, quinoline, isoquinoline, morphine, indole and purine systems. Some of the alkaloids are derived from aliphatic amines and belong to non-heterocyclic group. The alkaloids may be classified according to the presence of above mentioned systems, but such a systematic classification is not very rigid in the sense that is subjected to alter with the discovery of new alkaloids and availability of more physico-chemical data regarding the constitutions of the alkaloids. Some of the important alkaloids are classified as follows.[45]

Group	Examples
Pyrrole	Hygrine, Stachydrine
Pyridine	Coline, Nicotine
Tropane	Atropine, Cocaine
Quinoline	Quinine, Cinchonine
Isoquinoline	Papaverine, Narcotine
Morphine	Codeine, Morphine, Thebaine
Indole	Brucine, Harmine, Strychnine
Purine	Caffeine
Alkaloids derived from aliphatic amine	Damascerine, Hordenine

More than twenty five alkaloids have been isolated from the roots, stems and branches of Cinchona tree. The tree is known as 'fever tree', and it is a native of South America and cultivated extensively in Japan, Java and India. The most important members of the cinchona alkaloids are quinine and cinchonine. Cinchonine is similar to quinine, both contain an alcoholic OH group and readily form acetyl derivatives, and chlorocompounds on treatment with acetic anhydride and PCl_5. The only difference is that the methoxy group of quinine is replaced by hydrogen atom in cinchonine. Quinine (I)[46] consists of two ring systems.



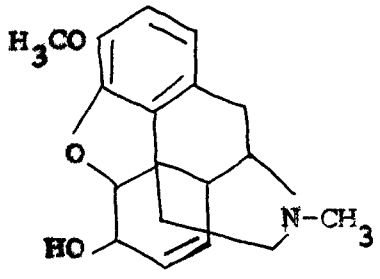
(I)

On the left is π-deficient heteroatomic nucleus with a 6-methoxy substituent. The upper right hand part contains a heteroparaffinic amine, the so called quinuclidine ring, the latter contributes most of the basic properties associated with alkaloids and like other heteroparaffines, it must have essentially the inert properties of triethyl amine. The two ring systems are joined by both being inserted into methanol, giving a secondary alcohol. The

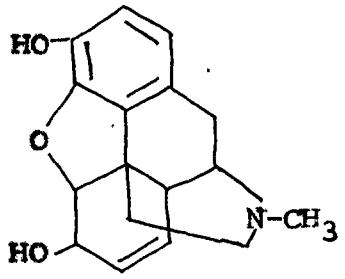
secondary alcoholic group and the vinyl group will combine to lower slightly the basic strength of a tertiary amine.

The first and second ionisation constant values of quinine are 8.4 and 4.7, respectively. The first value (8.4) corresponds to tertiary heteroparaffinic nitrogen and the second (4.7) to quinoline nitrogen. There seems no possibility of the columbic interactions produced due to the two basic nitrogens being too far apart.

The morphine family of alkaloids contains three important members codeine, morphine and thebaine[47], with the composition $C_{18}H_{21}O_3N$, $C_{17}H_{19}O_3N$ and $C_{19}H_{21}O_3N$, respectively. Morphine is a phenol and it may be methylated at the phenolic group to give codeine. Both these bases (codeine (II), and morphine (III)



(II)



(III)

also contain a secondary alcoholic group, OH which may be replaced by halogens. The alkaloids also contain a third oxygen atom which remarkably inactive under a variety of

in the range 3700-1540 cm^{-1} in dilute $CHCl_3$ solution. They reported the appearance of a strong band in the region 3625 - 3540 cm^{-1} with an apparent molecular extinction coefficient 30-160. This band was designated for the presence of hydroxyl group. Imino group present in an indole nucleus or secondary amido group, produces a sharp band in the region 3480 - 3440 cm^{-1} with an apparent extinction coefficient of 100 - 210. However, when the amino group is present in a piperidine ring, the absorption is much weaker, but may be observed at increased path length. The presence of carbonyl group in an alkaloid has been detected in the region 1780 - 1620 $cm.^{-1}$ Phenyl ring and aromatic nitrogen in the alkaloids have been found to give absorption bands in the regions 1640 - 1600 cm^{-1} and 1600 - 1500 $cm.^{-1}$ respectively. The presence of tertiary and secondary nitrogens in heterocyclic aromatic ring systems or less commonly in aliphatic ring systems in alkaloids made them capable for acting as potential coordinating ligands for metals specially those belonging to transition metals. The studies are not numerous apparently due to the complex structures of alkaloids and presence of more than one coordination sites in most of these compounds.

Most of the reference available in the chemical literature regarding the metal-alkaloid interactions belong

to the studies on the complexes of cinchona alkaloids specially cinchonine and quinine. Amongst the non - transition metals the double salts of $SbCl_5$ with cinchonine and quinine having the composition $C_{19}H_{22}ON_2 \cdot 2HCl \cdot SbCl_5$ and $C_{20}H_{24}O_2N_2 \cdot 2HCl\ SbCl_5\ 2H_2O$ and crystallising in light yellow prismatic forms have been reported by Thomson[50]. Dugenois[51] obtained complexes with CdI_2 of the types, $AH[CdI_3]$ and $(AH)_2[CdI_4]$ (where A = alkaloid). Subba Rau and Sahsadri[52] reported the organomercury compounds of quinine and cinchonine. According to these workers, a suitable combination of quinine and mercury may be expected to have the good features of mercury and quinine compounds. This combination may have a large utility range and may be less toxic. Ray[53] reported the preparation of compounds formed by the interactions of $Hg(NO_3)_2$ and alkaloids such as codeine, quinine, brucine, etc., and measured their conductivities. With quinaldine and $ReCl_3$ a paramagnetic (μ eff = 1.2 B.M) product $Re_2 \cdot (Quind)\ Cl_5$ has been reported.[54]

A relatively more detailed study of the interactions of alkaloids with transition metals has been carried out. Burrows and Turner[55] prepared the alkaloid complexes with ferrioxalate whereas Jakob Meisenheimer[56] and others prepared rose needle shaped optically inactive complexes of

Cr(III) with cinchonine and quinine. Red needles of cinchonine salts were obtained by boiling cis or trans pyridinum-di-oxalodiaquochromate with cinchonine or quinine. A dirty green Cr(III) complex, Na $[Cr(C_2O_4)_2 (cinch)_3] 5H_2O$ results on boiling a mixture of sodium dioxalodiaquodi-chromate and cinchonine. Complexes of $CoCl_2$ and $CuCl_2$ with cinchonine, quinine and other alkaloids were reported by Vascantanu and Jurca[58] who isolated the complexes of the type, (cinch) $CuCl_2.H_2O$ and(quin) $CuCl_2 2H_2O$, and $(cinch)_2 \cdot (CoCl_2)_3$. Frausto et al.[59] reported Ag complexes of cinchona alkaloids and calculated dissociation, and the stability constants of these complexes of the general formula Ag_xHyL_x (L = alkaloid) by employing potentiometric titrations at 20^oC.

The work described in this thesis is concerned with the studies on the transition metals complexes of aminoacids and the alkaloids. This piece of research work involves investigations carried out to explore further, the developing branch of coordination chemistry associated with the metal-natural products complexes. This consists of two systems, one dealing with aminoacids and the other comprising of naturally occurring complex nitrogeneous compounds of vegetable origin known as alkaloids.

The complex chemistry of aminoacids has been developed to a remarkable extent as indicated by the scores of papers published in recent years, covering various aspects of this field. However, one aspect of metal-aminoacids interactions is yet untouched, which is related to the study of the complexes of aminoacids with metals having unstable or abnormal oxidation states e.g., Ti(III), Cr(II), Cu(I), VO^{2+} and UO_2^{2+}. The studies in this system include the determination of the composition of the complexes in solution by the electrometric methods and the evaluation of stability constants from the data of pH-metric titrations based upon Bjerrum's method. The other aspect of this problem concerning with aminoacid complexes is the measurement of the solubility of copper(I) iodide in potassium iodide solution in presence of various aminoacids and subsequent determination of the composition of Cu(I) aminoacid complexes. The most interesting study in aminoacid system consists of the rate law studies on the substitution reactions of aminoacids with tetrakis-(thiourea) palladium(II) chloride. The kinetic studies were carried out spectrophotometrically by measuring the absorption with time. The rate law follows the expression.

$$K_{obsd.} = k_1 + k_2 [L]$$

the values of k_1 and k_2 are found out from the linear plots of $K_{obsd.}$ versus concentrations of aminoacid. The values of

$K_{obsd.}$ are correlated with the pK_a and dissociation constants of aminoacids and formation constants of the complex.

The metal-alkaloids interaction studies have not yet been paid enough attention due to the complex structures of alkaloids and difficulty in isolating the complexes in pure states. A very few data are reported in literature regarding the infra-red of the alkaloids. The work presented in this manuscript deals with the studies on the interaction of alkaloids with transition metal ions. The complexes have been isolated and characterised, and their structures have been discussed on the basis of detailed study of the infra-red spectra of the alkaloids and their complexes.

The work described in the proceeding pages consists of the studies on the followings.

1. Determination of the composition of the complexes of Cr(II), Ti(III), VO^{2+}, and UO_2^{2+} with aminoacids such as glycine, L-asparagine, L-leucine, DL-serine, DL-valine, L-proline, DL-α-alanine, β-alanine, cysteine, methionine and taurine, using potentiometric and conductometric methods.
2. The evaluation of stability constants of the aminoacid complexes from the data of the pH-metric titration using Bjerrum's method.

3. The determination of the composition of the complexes of copper(I) iodide with aminoacids such as glycine, L-leucine and L-proline using the solubility data obtained from the solubility measurements of Cu_2I_2 in aqueous potassium iodide in presence of above aminoacids.

4. Kinetic studies on the substitution reactions of tetrakis (thiourea) palladium(II) chloride with various aminoacids such as glycine, DL-α-alanine L-leucine, L-proline, DL-serine, DL-valine and DL-threonine in aqueous solutions.

5. Isolation of the complexes of alkaloids such as brucine, codeine, quinaldine and quinine with Cu(I), Ti(III), VO^{2+}, UO_2^{2+}, Co(II), Cu(II), Ni(II), Cr(III) and Mn(II).

6. Assessment of the structures and the nature of the bonding in the alkaloid complexes from the interpretations of the infra red spectra of the alkaloids and their complexes.

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C H A P T E R - I:

STUDIES ON THE COMPLEXES OF CHROMIUM(II) CHLORIDE TITANIUM (III) CHLORIDE,OXOVANADIUM (IV) SULPHATE AND OXOURANIUM (VI) SULPHATE WITH SOME AMINO ACIDS

I N T R O D U C T I O N

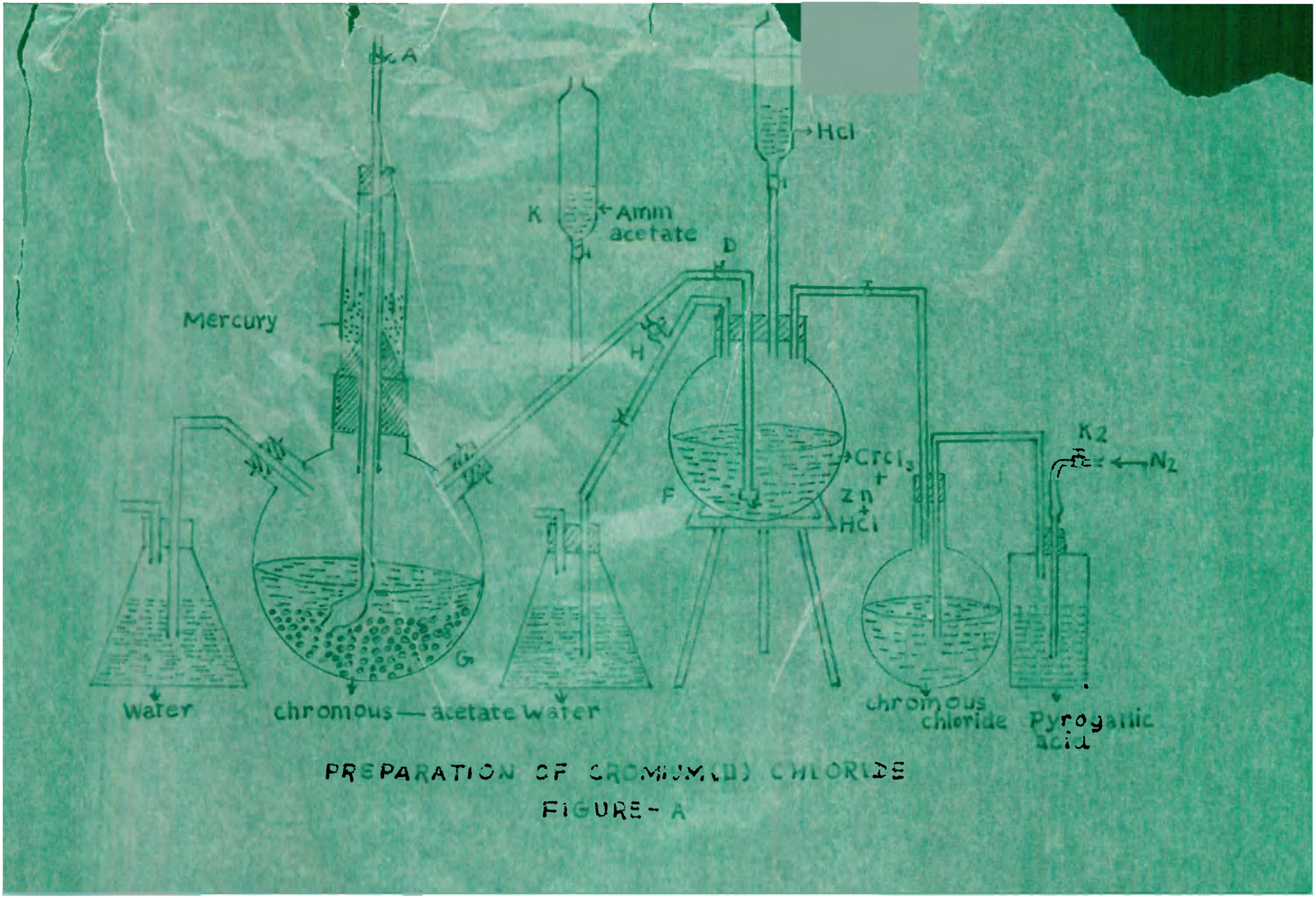
The study of transition metal complexes with amino-acids has been a subject of extensive research in recent years. The interest in the investigations concerning the coordination chemistry of aminoacids arises, because of the biological importance of this family of compounds and the presence of potential amino and carboxylic groups, and in some cases still more reactive substituents.

The earlier work on aminoacids complexes was pioneered by Ley[1,2] who studied the interaction of copper(II) and nickel (II) ions with various ∝-aminoacids. These studies were limited mainly to the isolation of the complexes and their electrolytic behaviour in solution determined from conductivity measurements. For a long time, the domain of the studies was limited only to the determination of the composition of the complexes by physico-chemical methods. However, with the advent of the remarkable work of Bjerrum[3] on the stability of the complexes in late thirties and early forties, a major break through took place in the field of metal - aminoacids chemistry. The main bulk of the work published during the last two decades, is mainly oriented towards the quantitative aspects of the stability of the aminoacid complexes. Amongst the papers appeared in literature during the early fifties, regarding the afore aspects of metal-aminoacid complexes, the work of Albert[4] is worth mentioning.

Inspired by Bjerrum's theoretical formulations, Albert derived some simpler equations to calculate the dissociation and stability constants of aminoacids and their complexes, respectively. Employing methods of pH-metric and potentiometric titrations, he calculated the stability constants of a large number of metal complexes with various aminoacids and concluded that the reactivities of the various aminoacids towards a metal ion were dependent on the stability of the complexes, and ionization constants. The recent work on aminoacid complexes is the result of some illuminating studies carried out by a band of electrochemists, including Monk[5] (solubility behaviour), Doody[6] (polarographic methods), Tanford[7] (e.m.f.measurements) and various others[8-14] who made some important contributions to the metal - aminoacids coordination chemistry.

A survey of the existing literature indicates that no attempt has yet been made to study the aminoacid complexes with metal ions in their abnormal oxidation states. The studies described in this chapter are, therefore, carried out by keeping in view the above fact and are related to the interactions of aminoacids such as glycine, L-asparagine, DL-α-alanine, β-alanine, DL-valine, DL-serine, L-proline, L-leucine, DL-leucine, DL-methionine,

cysteine and taurine with chromium (II), titanium(III), oxovanadium (IV) and oxouranium (VI) ions. The compositions of the complexes have been determined by the potentiometric and conductometric methods, and the stabilities have been computed from the results of pH-metric titrations.



PREPARATION OF CROMIUM(II) CHLORIDE

FIGURE - A

EXPERIMENTAL

Preparation and standardisation of chromium(II) chloride

Since the behaviour and stability of the chromium(II) chloride solution are likely to vary from sample to sample depending upon the mode of preparation, the amount of acid present, the extent of dilution and the methods of storage. A specific method has to be adopted for the preparation and storage of chromium(II) chloride. The method proposed by Bathis and Bailer[15], and checked by Dutton[16] was followed. Chromium (III) chloride was reduced with zinc and hydrochloric acid, and the chromium(II) chloride, thus formed was converted into chromium(II) acetate. The acetate was decomposed by (A.R.grade) hydrochloric acid (quantity as minimum as possible) to the chloride. The dry and pure hydrogen chloride gas was passed and the crystals of chromium (II)chloride tetrahydrate were obtained.

An apparatus shown in fig. A was assembled. About 60 gms of (A.R.grade) $CrCl_3$ was dissolved in 70 ml of distilled water and transferred to a round bottom flask F containing about 100 gms of granulated zinc pieces. About 140 ml of conc. HCl was allowed to drop on the mixture, and the $CrCl_3$ was reduced to bright blue chromium(II) chloride. When the evolution of hydrogen slackened,

stopcock D was opend and the rubber connection H was closed by means of a pinchcock, so that the pressure of hydrogen forces the solution in-to the flask G. The flask G was deaerated by passing oxygen free dry nitrogen gas through the stopcock D before transferring the solution from flask F to G. A filtered solution of 168 gms of sodium acetate (B.D.H.A.R.) in 100 ml of air free doubly distilled water was introduced into the reaction flask G through the separating funnel K, and the mixture was stirred regularly. The dark red precipitate of chromium(II) acetate was formed and it was allowed to settle down. The supernatant liquid was filtered off by means of suction pump attached to the stirrer. The precipitate was washed with air free doubly distilled cold water. The chromium(II) acetate, thus produced was dissolved in cold HCl added in small drops from a dropping funnel with continuous shaking to avoid the excess of free hydrochloric acid. The solution was kept in a freezing bath and a current of dry and pure hydrogen chloride gas was passed for about an hour by means of a Y tube attached to the stopcock A. Blue crystals of $CrCl_2\ 4H_2O$ were precipitated in the reaction flask. The supernatant liquid was filtered off, and the precipitate was washed with ice cold dilute HCl, dry acetone, and finally with dry ether to remove the excess of HCl and acetone. The blue crystals were dissolved in ice cold air

free doubly distilled water (minimum quantity). An atmosphere of pure and dried nitrogen (purified by passing through alkaline pyrogallol and chromium(II) chloride solutions) was kept during the preparation of chromium(II) chloride. A layer of kerosene oil was always kept over the protective chromium(II) chloride solution in the storage flask (Fig.B), and the atmosphere of dry and pure nitrogen was created to avoid the oxidation of chromium (II) chloride.

Standardisation of chromium (II) chloride:

Although the direct titrations of dichromate ion in 3 to 5% sulphuric acid has been recommended for the standardisation by a number of workers.[17,18,19] Lingane and Pecsock[20] have reported the inadequacy of the method. They pointed out that the dichromate - chromic ion couple does not function reversibly, so that the titration curve at the equivalence is very asymmetrical and no warning of the approach of the end point is obtained. Hence Rienacker[21]'s method of titration with copper sulphate was followed. 100 ml of 0.1N cupric sulphate (A.R. B.D.H) solution and 10 ml of conc. A.R. grade hydrochloric acid were taken in an air tight cell. It was covered with a thick layer of kerosene oil and the solution was deaerated by passing oxygen free

dried nitrogen gas for about ten minutes. The indicator electrode used was platinum electrode in conjugation with saturated calomel (S.C.E.) as a reference electrode. The solution of copper sulphate was kept covered with layer of kerosene oil and the tip of burette in the cell was kept below the layer of kerosene oil. The change in potential was recorded after each successive addition. The experimental data are given in table 1.

T A B L E NO. I:

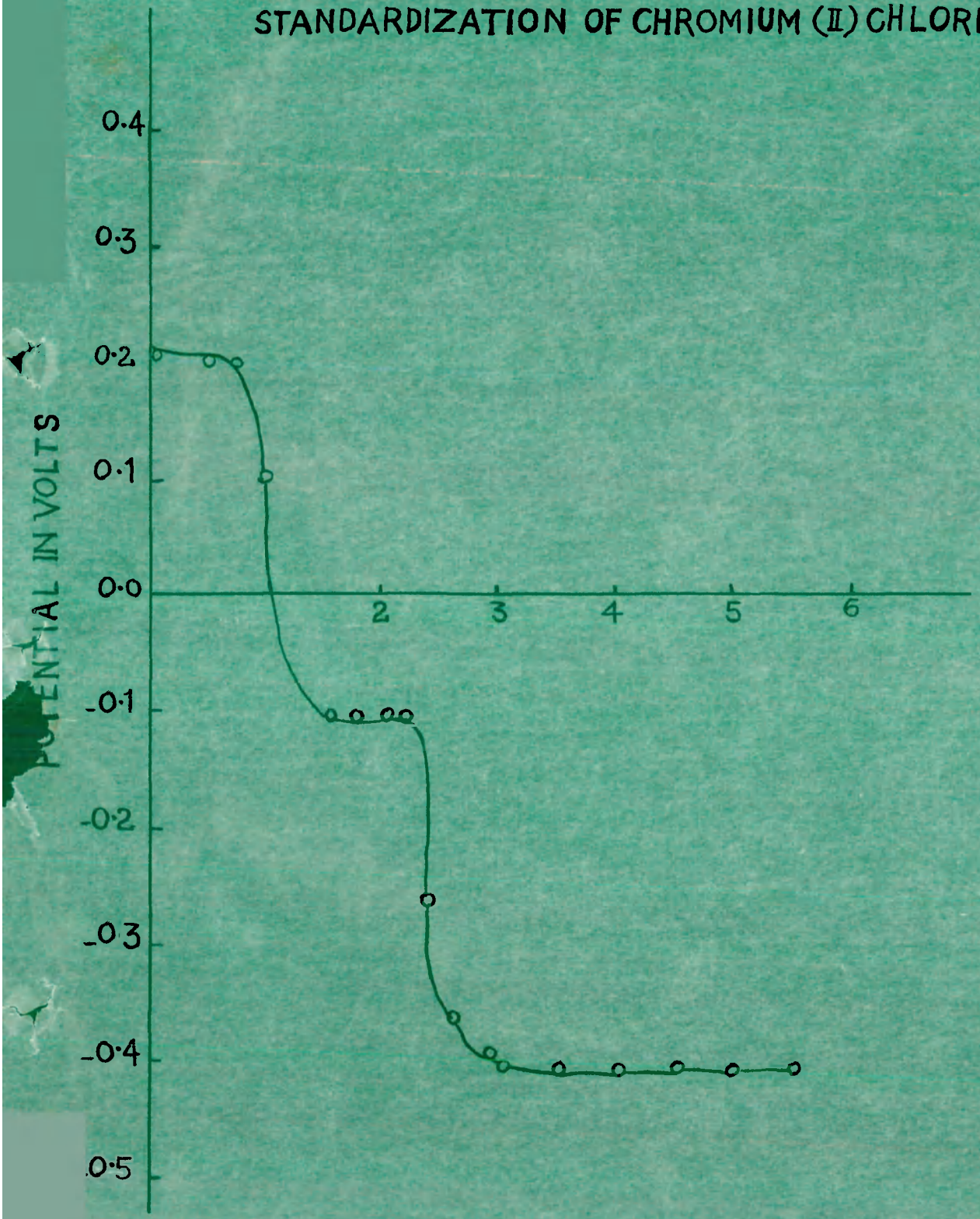
Vol.of chromium(II) chloride in ml.	Potential in volts.
0.00	+0.2090
0.50	0.2048
0.75	0.2040
1.00	1.0040
1.50	-0.1035
1.75	0.1045
2.00	0.1048
2.20	0.1051
2.40	0.2065
2.60	0.3062
2.80	0.3092
3.00	0.4030
3.50	0.4045
4.00	0.4060
4.50	0.4065
5.00	0.4072

The titer value from the curve = 3 ml
strength of chromium(II) chloride = 0.33M

(Vide Fig. No. I)

FIGURE No. 1

STANDARDIZATION OF CHROMIUM (II) CHLORIDE



VIDE TABLE No. 1

Chemicals :

All the aminoacids i.e., glycine, β-alanine, DL-α-alanine, L-proline, DL-serine, L-leucine, L-asparagine, DL-valine, DL-methionine, taurine and cysteine (biologically pure products) were obtained from B.D.H. (England). Standard solutions of aminoacids were prepared in doubly distilled air free water by dissolving the calculated amounts of the reagents. These solutions were covered with a layer of toluene to avoid the direct contact of air, and were stored in cold.

Potassium hydroxide solution was prepared by dissolving carbonate free (A.R. B.D.H. grade)potassium hydroxide crystals in air free doubly distilled water. The solution was standardized by titrating it against 0.1N oxalic acid. The solution was stored in a Pyrex bottle fitted with a guard tube containing KOH and $CaCl_2$ to check moisture and carbondioxide. The strength of the solution was checked on the eve of each titration in a particular set.

Uranylsulphate and vanadylsulphate (B.D.H.A.R.) were employed during the experiments. The metal contents in the aqueous solutions were estimated gravimetrically as the metal oxides.[22,23]

Preparation and standardisation of titanium(III) chloride:

About 150 ml solution of titanous chloride (12.5% W/V solution containing 12.5% HCl, M & B product, England) was taken in a conical flask and about 10 gms of pure 99.5% titanium metal sponge (Jhonson, Matthey, London) was added to it. Dry HCl gas was passed into the solution for about 10 minutes, and the flask was heated on a water bath. The metal reacts with the acid producing titanous chloride and evolving hydrogen. The two processes were alternately repeated till all the particles of the metal underwent dissolution. The solution was covered with a layer of ether, cooled in a freezing mixture and saturated with hydrogen chloride gas, when violet $TiCl_3$ $6H_2O$ crystallised.[24] The crystals were repeatedly washed with air free conductivity water, and then the solution was made. The solution was always kept covered with a layer of toluene in a flask wrapped in a black paper. An aqueous solution of titanium (III) chloride was prepared by dissolving crystals of $TiCl_3$ $6H_2O$ in air free doubly distilled water and standardised[25] by adding a known amount of it to an excess of pure ferric alum solution containing sulphuric acid, and titrating the resulting ferrous sulphate against standard potassium permanganate solution. Fresh

solutions were always prepared before use and kept covered with a layer of kerosene oil or toluene throughout the investigations to avoid oxidation.

Apparatus :

The potentiometric titrations were carried out using a Tinsley potentiometer with lamp and scale arrangements using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were made with a direct reading EIL-meter model 23 A (England) using glass and saturated calomel electrodes. All titrations were carried out in specially designed cell with provision for transferring the chromium(II) chloride from the storage bottle, and passing oxygen free nitrogen for stirring the solutions. The concentrations of the chromium(II) chloride and titanous chloride solutions were checked before the study of the each system. The conductometric titrations were performed using a Philips Conductometer model PR 9500 (India) and a dip type conductivity cell (cell factor = 1.48).

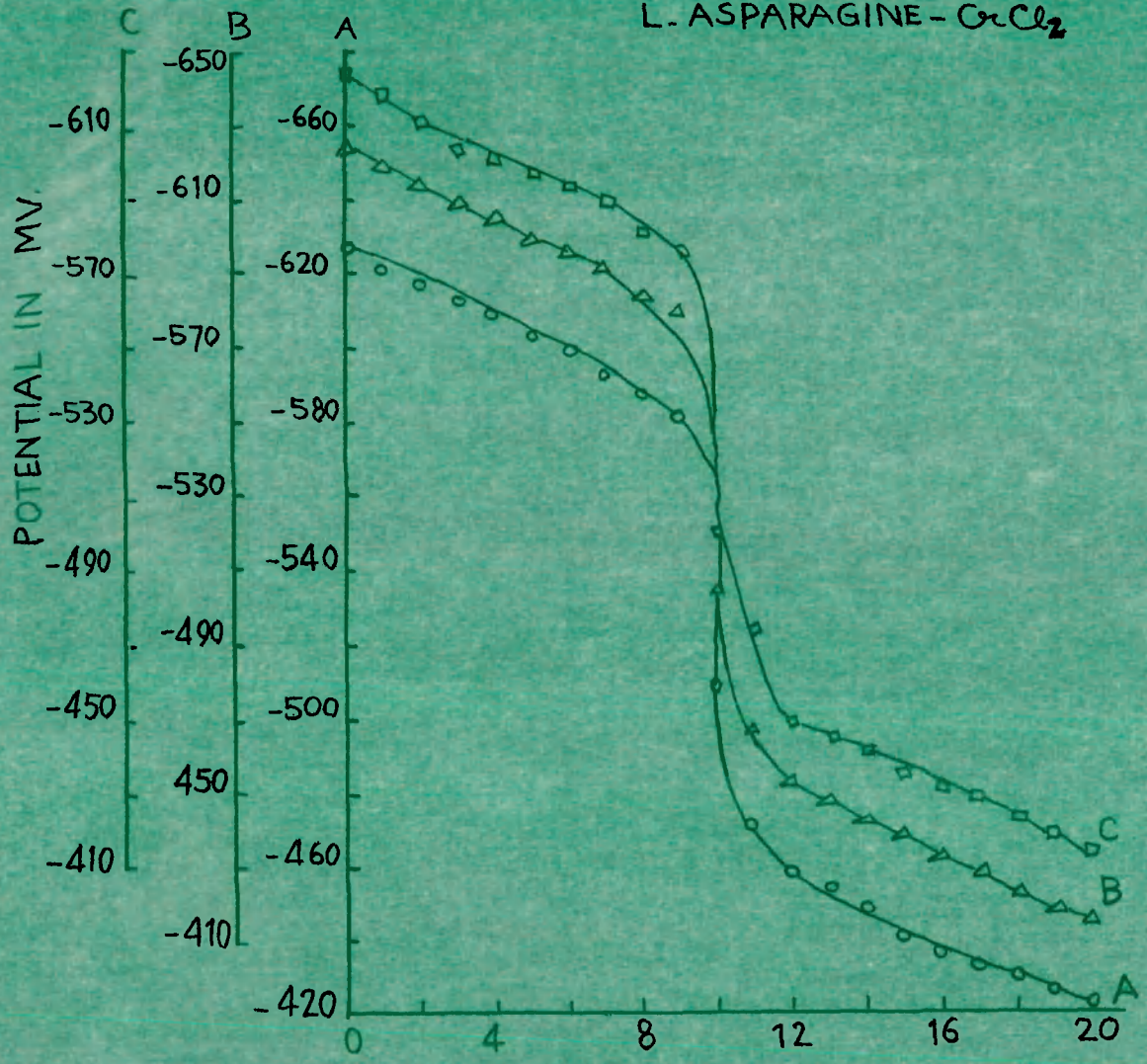
T A B L E No. 2 A

Potentiometric titrations of Chromium(II) Chloride against L - Asparagine

Vol.of L-Asparagine added. (ml)	1st. Titration. A	2nd. Titration. B	3rd. Titration. C
1	2	3	4
		Potential in mv	
0	-628	-625	-624
1	622	620	618
2	619	615	612
3	613	610	606
4	610	606	602
5	604	600	598
6	600	596	594
7	594	592	590
8	588	584	580
9	582	580	576
10	509	504	500
11	470	466	464
12	458	452	448
13	454	448	440

(Contd.)

FIGURE NO. 2A
POTENTIOMETRIC TITRATIONS.
L-ASPARAGINE - $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M L-ASPARAGINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ VS. 20 ml OF 0·05 M L-ASPARAGINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M L-ASPARAGINE (FROM BURETTE)

VIDE TABLE NO. 2A

1	2	3	4
14	448	442	434
15	440	438	430
16	436	432	428
17	432	428	422
18	430	422	418
19	426	418	416
20	422	416	412

1st.titration :- 10 ml of 0.066M Chromium (II) Chloride against 20 ml of 0.066M L- Asparagine (from burette).

2nd.titration :- 10 ml of 0.05M Chromium (II) Chloride against 20 ml of 0.05M L-Asparagine (from burette)

3rd.titration :- 10 ml of 0.04M Chromium (II) Chloride against 20 ml of 0.04M L-Asparagine (from burette).

(Vide Fig. No.2 A)

T A B L E No.3 A

Potentiometric titrations of Chromium(II) Chloride against DL-α-Alanine

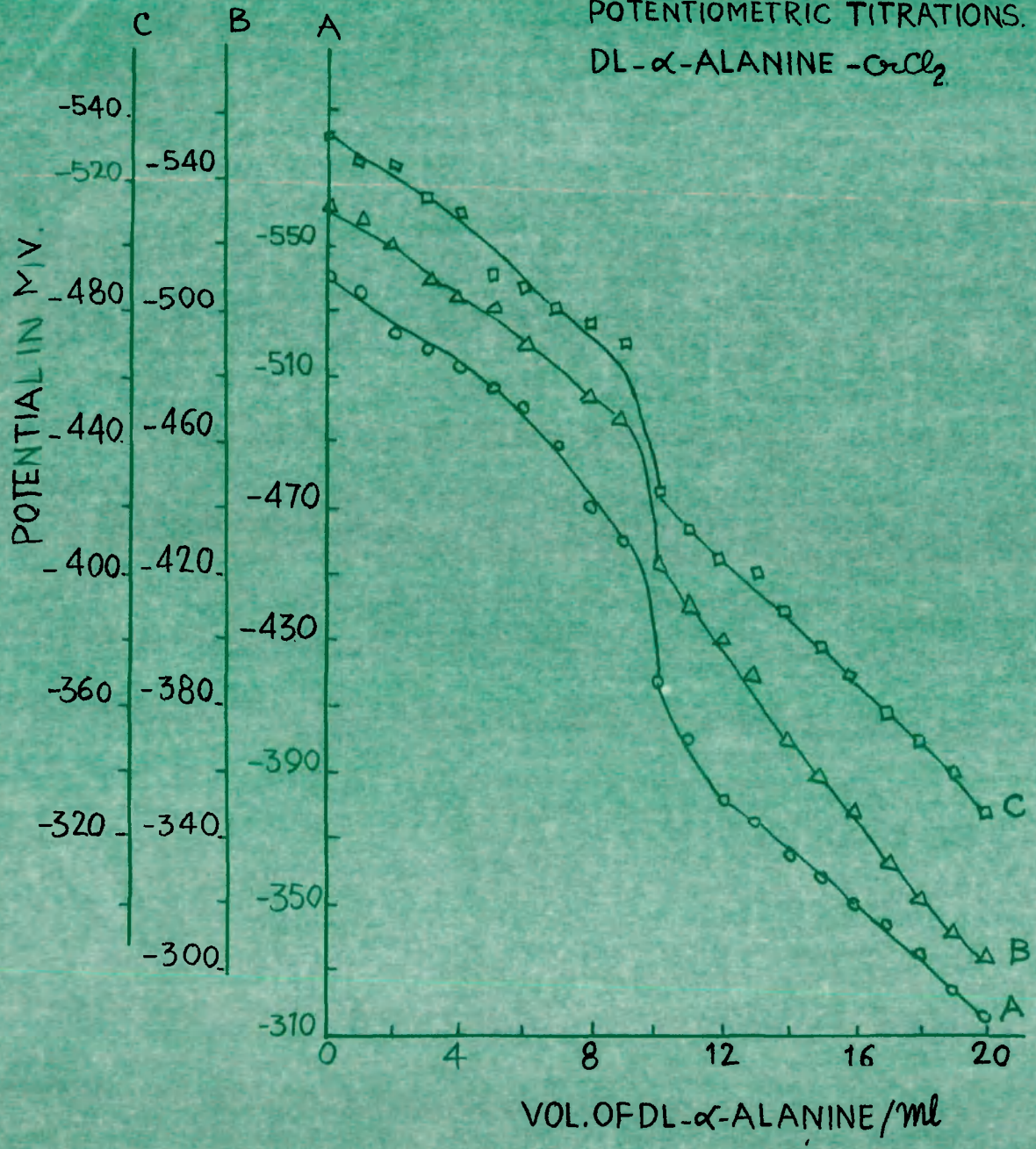
Vol. of DL- Alanine added (ml)	1st.Titration.	2nd.Titration.	3rd.Titration.
	A	B	C
1	2	3	4
	Potential in mv		
0	-540	-532	530
1	536	528	526
2	522	520	524
3	518	510	514
4	512	504	500
5	506	500	490
6	500	488	486
7	482	478	480
8	470	472	476
9	460	468	470
10	418	422	424
11	400	410	414
12	382	400	404
13	374	385	400

(Contd.)

FIGURE NO. 3A

POTENTIOMETRIC TITRATIONS.

DL-α-ALANINE - $CrCl_2$



A = 10 ml OF 0·066M $CrCl_2$ Vs. 20 ml OF 0·066M DL-α-ALANINE (FROM BURETTE)

B = 10 ml OF 0·05M $CrCl_2$ Vs. 20 ml OF 0·05M DL-α-ALANINE (FROM BURETTE)

C = 10 ml OF 0·04M $CrCl_2$ Vs. 20 ml OF 0·04M DL-α-ALANINE (FROM BURETTE)

VIDE TABLE NO. 3A

1	2	3	4
14	364	368	389
15	358	358	378
16	350	348	368
17	344	332	358
18	334	320	350
19	324	310	340
20	316	304	328

1st.titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M DL-α-Alanine (from burette).

2nd.titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M DL-α-Alanine (from burette).

3rd.titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M DL-α-Alanine (from burette).

(Vide Fig.3 A)

T A B L E No.4 A

Potentiometric titrations of Chromium(II) Chloride against β-Alanine

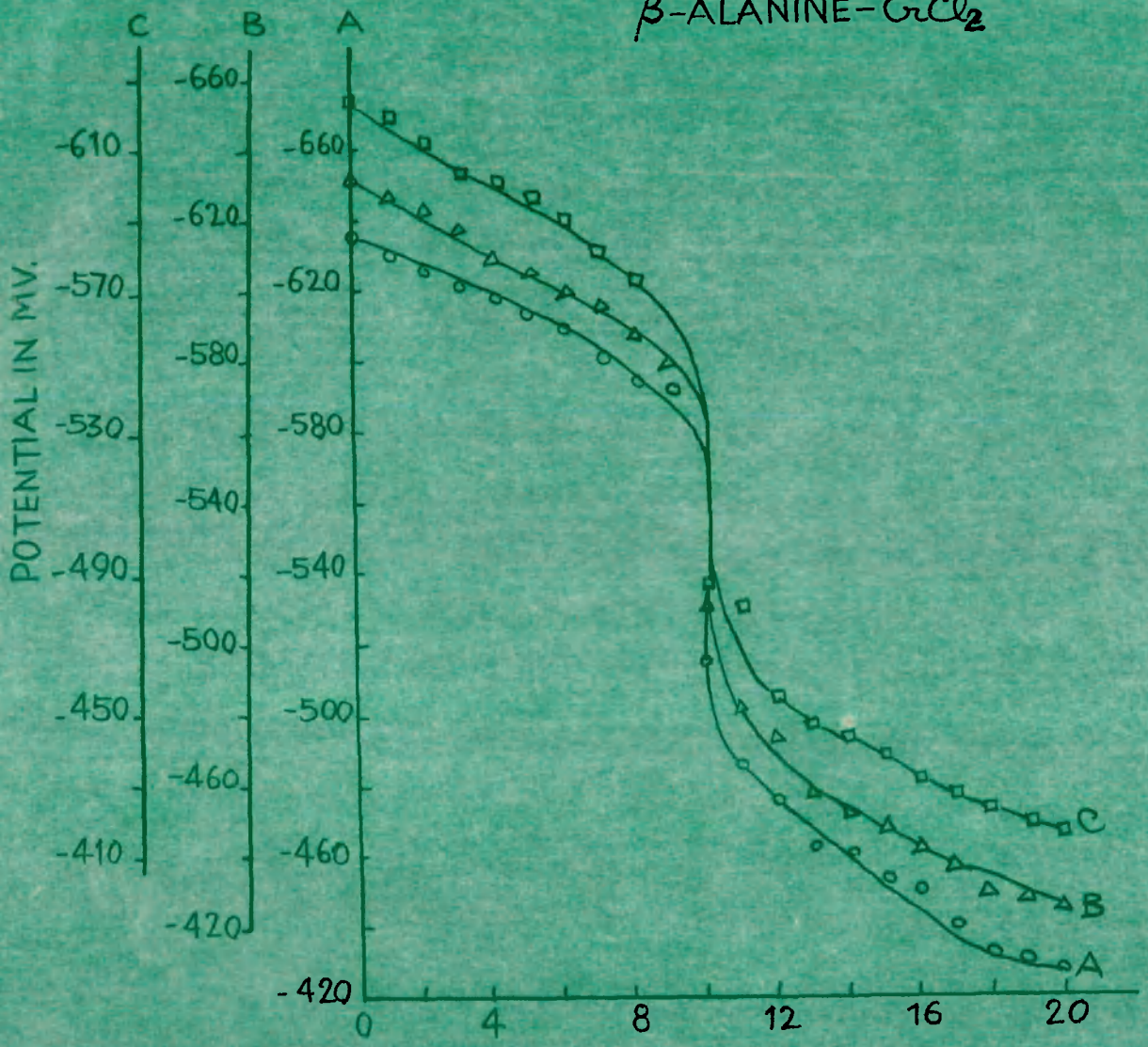
Vol. of β-Alanine added.(ml.)	1st. Titration.	2nd. Titration.	3rd. Titration.
	A	B	C
1	2	3	4
		Potential in mv	
0	-636	-632	-624
1	630	628	620
2	626	624	612
3	622	618	604
4	618	610	602
5	614	606	598
6	610	600	590
7	600	594	582
8	596	588	574
9	592	580	508
10	516	512	478
11	486	482	472
12	476	474	456
13	462	459	448

(Contd.)

FIGURE NO. 4A

POTENTIOMETRIC TITRATIONS.

β-ALANINE – $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M β-ALANINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M β-ALANINE. (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ VS. 20 ml OF 0·04 M β-ALANINE (FROM BURETTE)

VIDE TABLE NO. 4A

1	2	3	4
14	460	452	446
15	454	448	440
16	450	442	432
17	440	437	428
18	432	430	424
19	430	428	420
20	428	426	418

1st. titration:- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M β-Alanine (from burette).

2nd. titration:- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M β-Alanine (from burette).

3rd. titration:- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M β-Alanine (from burette).

(Vide Fig.No. 4 A)

T A B L E No.5 A

Potentiometric titrations of Chromium(II) Chloride against Glycine.

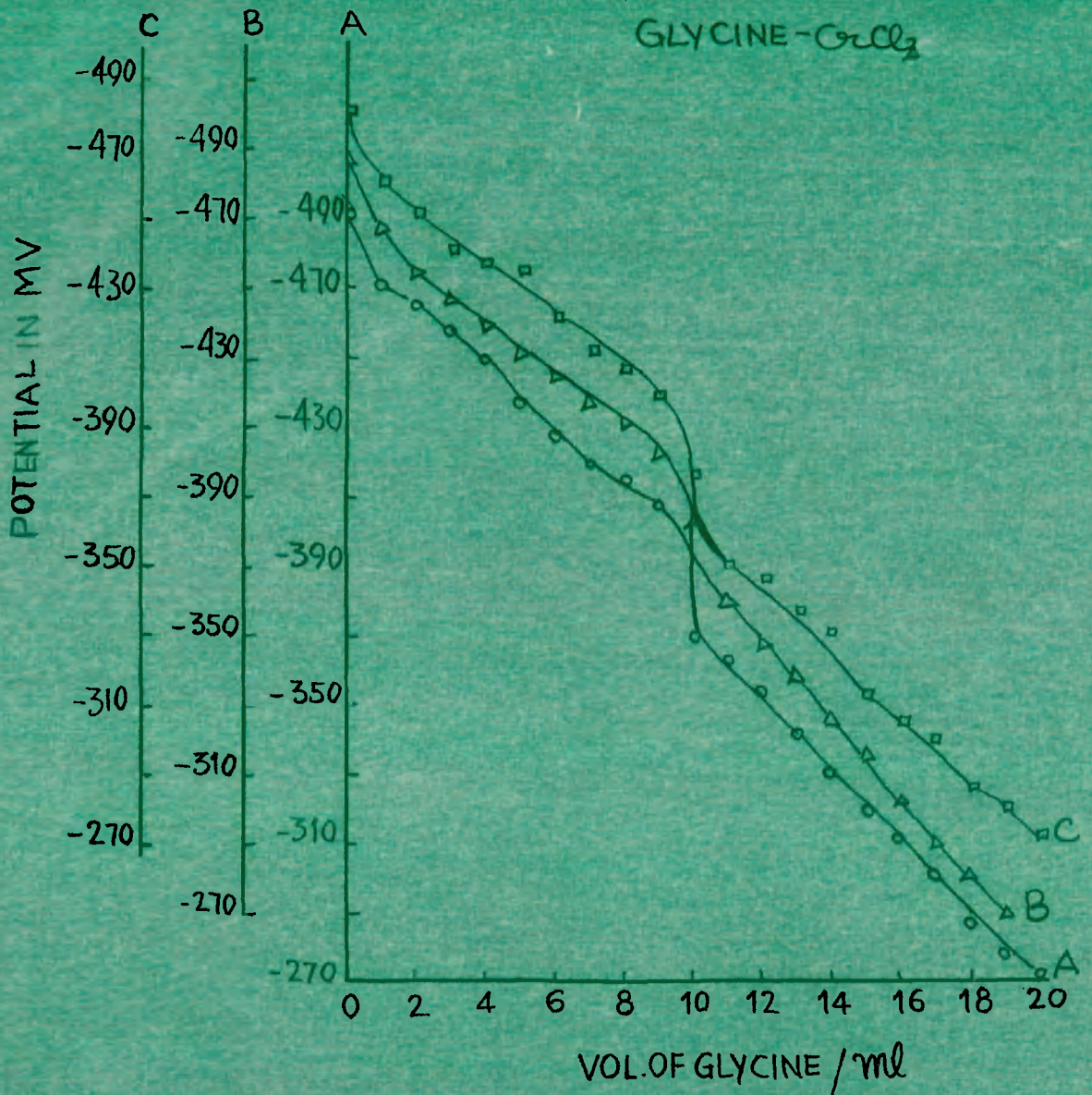
Vol. of Glycine added (ml)	1st. Titration. A	2nd. Titration. B	3rd. Titration. C
		Potential in mv	
0	-492	-488	-482
1	472	468	460
2	466	456	452
3	458	448	442
4	450	440	438
5	438	432	436
6	428	425	422
7	420	418	412
8	416	412	408
9	408	404	400
10	370	382	376
11	364	361	350
12	354	350	348
13	342	340	337
14	330	326	332
15	320	316	312

(Contd.)

FIGURE NO. 5A

POTENTIOMETRIC TITRATIONS

GLYCINE - $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M GLYCINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M GLYCINE (FROM THE BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M GLYCINE (FROM BURETTE)

VIDE TABLE NO. 5A

1	2	3	4
18	288	290	286
19	278	281	280
20	270	274	272

1st. titration:- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M Glycine (from burette).

2nd. titration:- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M Glycine (from burette).

3rd. titration:- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M Glycine (from burette).

(Vide Fig. No.5 A)

T A B L E No.6 A

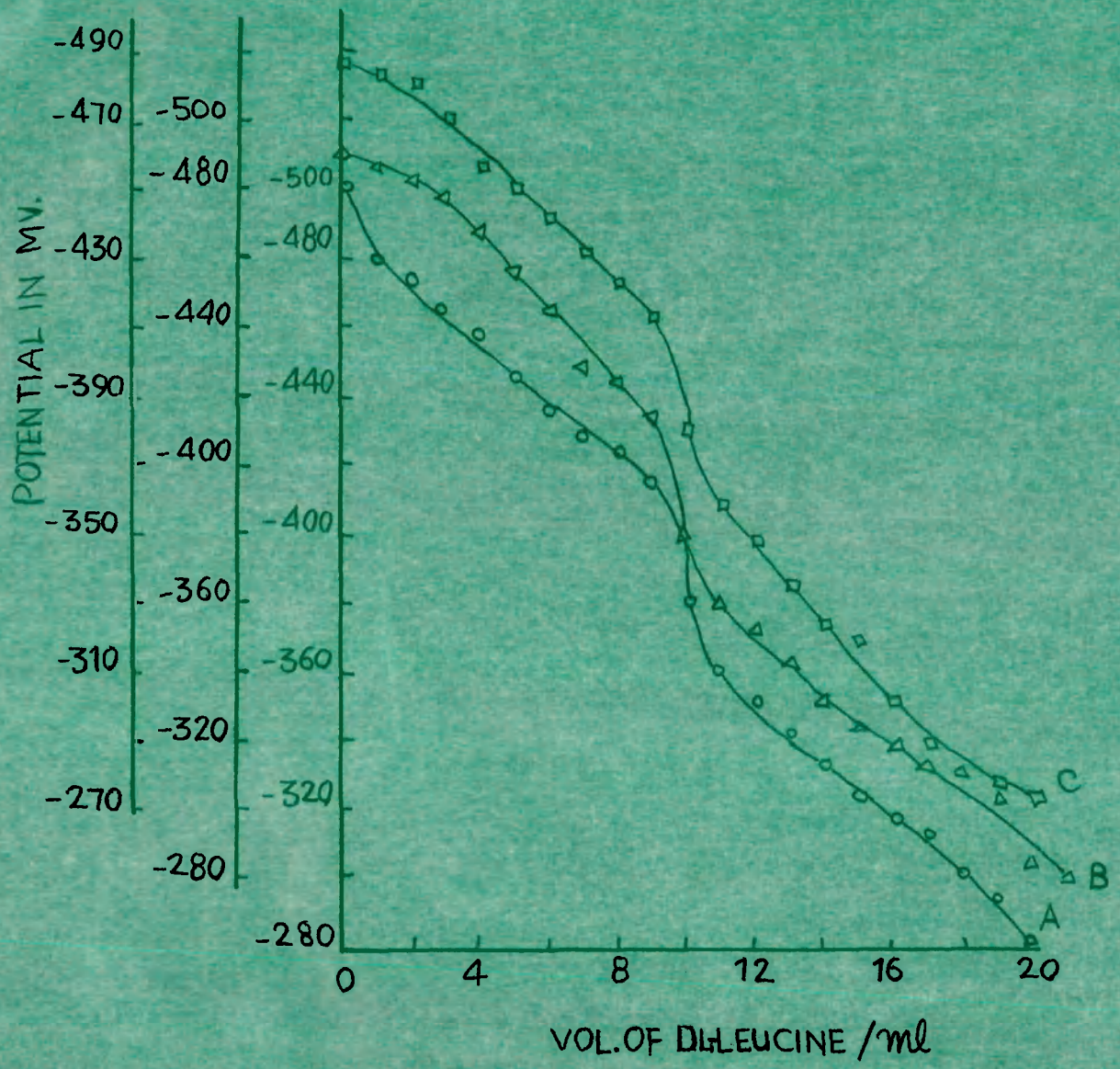
Potentiometric titration Chromium(II) Chloride against DL-Leucine

Vol.of L-Leucine added.(ml)	1st.Titration A	2nd.Titration B	3rd.Titration C
		Potential in mv	
0	-500	-490	-486
1	480	487	484
2	474	484	480
3	466	478	470
4	458	468	456
5	446	456	450
6	434	444	440
7	428	438	430
8	424	434	422
9	416	428	412
10	380	388	380
11	360	370	358
12	352	362	348
13	342	348	336

(Contd.)

FIGURE NO. 6A

POTENTIOMETRIC TITRATIONS.



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M DL-LEUCINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M DL-LEUCINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M DL-LEUCINE (FROM BURETTE)

VIDE TABLE NO. 6A

1	2	3	4
14	332	330	324
15	324	320	318
16	318	310	300
17	312	306	288
18	300	300	280
19	284	288	276
20	280	280	274

1st.titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of DL-Leucine (from burette).

2nd.titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M DL-Leucine (from burette).

3rd.titration :- 10 ml of 0.04M Chromium(II) Chloride against of 0.04M DL-Leucine (from burette).

(Vide Fig. No.6 A)

T A B L E No.7 A

Potentiometric titrations of Chromium(II) Chloride against L- Proline

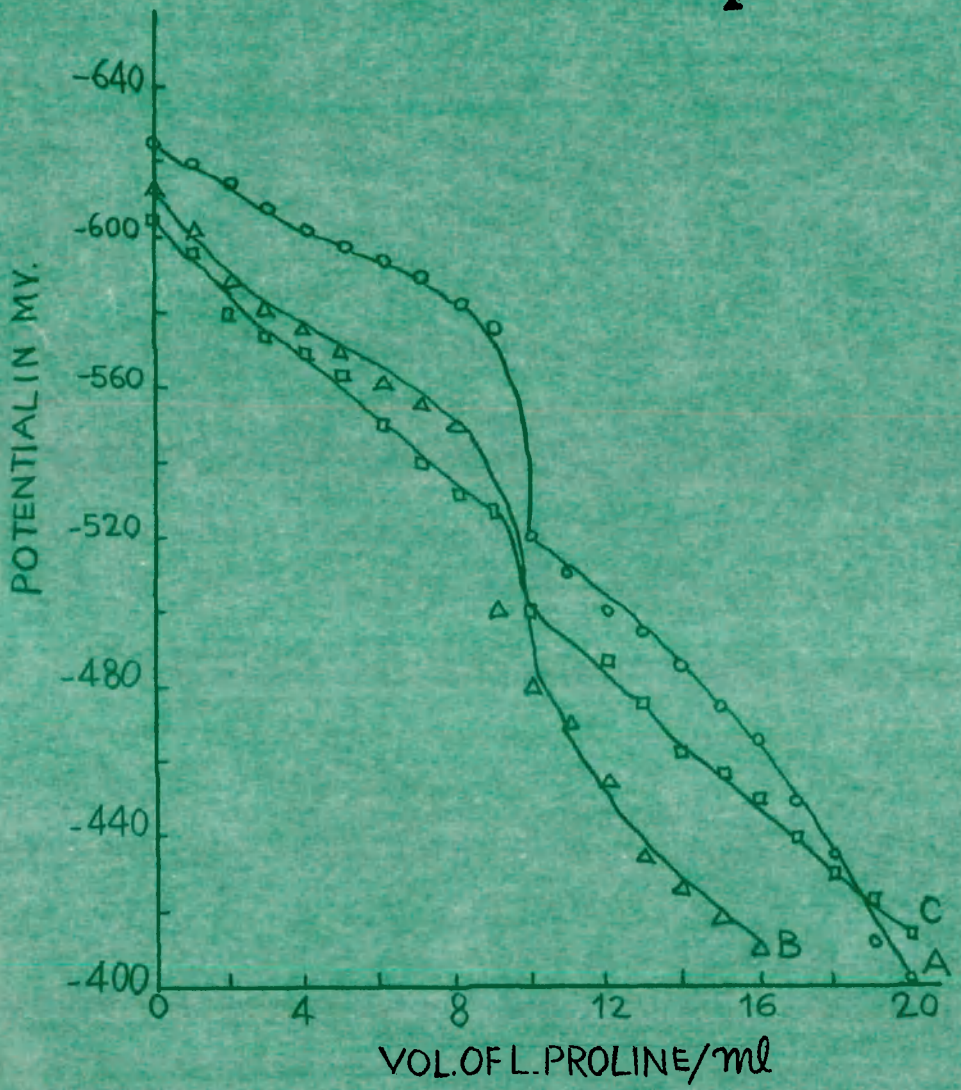
Vol.of L-Proline added.(ml)	1st.Titration. A	2nd.Titration. B	3rd.Titration. C
1	2	3	4
	Potential in mv		
0	-625	-612	-606
1	620	600	598
2	614	588	580
3	608	580	576
4	602	576	570
5	598	570	566
6	594	560	550
7	590	556	554
8	582	550	532
9	576	500	528
10	520	480	501
11	510	470	498
12	500	455	488
13	485	435	476

(Contd.)

FIGURE NO. 7A

POTENTIOMETRIC TITRATIONS.

L-PROLINE-$CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M L-PROLINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M L-PROLINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M L-PROLINE (FROM BURETTE)

VIDE TABLE NO. 7A

1	2	3	4
14	475	428	462
15	465	420	458
16	450	410	450
17	435	400	440
18	418	394	430
19	410	390	424
20	400	386	414

1st.titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M L-Proline (from burette).

2nd.titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M L-Proline (from burette).

3rd.titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M L-Proline (from burette).

(Vide Fig. No.7 A)

T A B L E No.8 A

Potentiometric titrations of Chromium(II) Chloride against DL-Serine

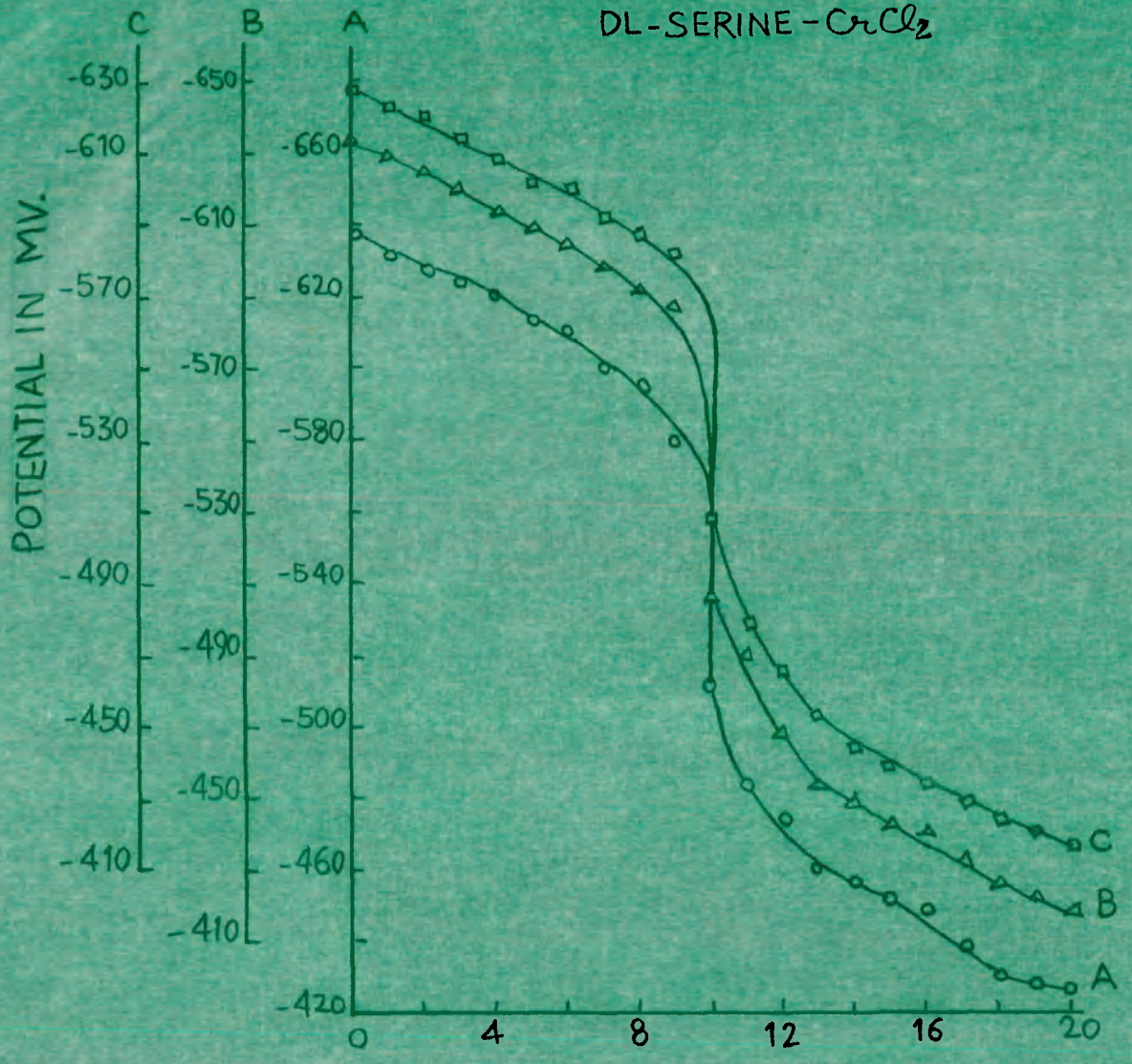
Vol.of DL-Serine added.(ml)	1st.Titration. A	2nd.Titration. B	3rd.Titration. C
1	2	3	4
		Potential in mv	
0	-638	-634	-628
1	632	630	624
2	629	626	620
3	625	620	614
4	620	614	608
5	615	610	602
6	611	606	600
7	600	598	592
8	595	592	588
9	580	588	582
10	510	506	508
11	484	480	478
12	474	468	464
13	460	454	452

(Contd.)

FIGURE NO. 8A

POTENTIOMETRIC TITRATIONS

DL-SERINE - $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M DL-SERINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M DL-SERINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M DL-SERINE (FROM BURETTE)

VIDE TABLE NO. 8A

1	2	3	4
14	457	448	444
15	452	442	438
16	448	440	434
17	438	432	428
18	430	426	424
19	428	422	420
20	426	418	416

1st. titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M DL-Serine (from burette).

2nd. titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M DL-Serine (from burette).

3rd. titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M DL-Serine (from burette).

(Vide Fig. No.8 A)

TABLE No.9 A

Potentiometric titrations of Chromium(II) Chloride against DL-Valine

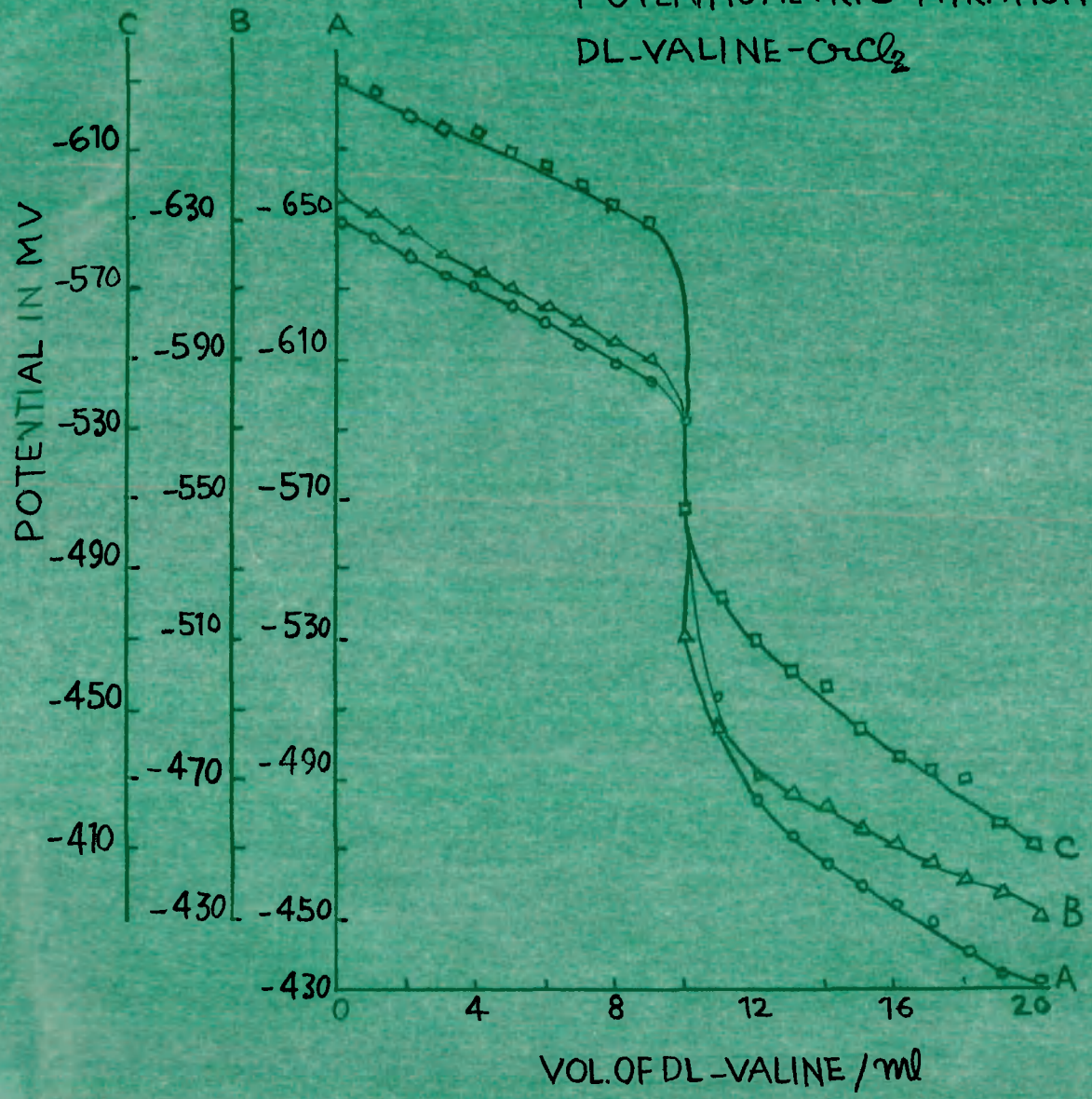
Vol.of DL-Valine added.(ml)	1st.Titration. A	2nd.Titration. B	3rd.Titration. C
1	2	3	4
	Potential in mv.		
0	-650	-635	-630
1	646	632	628
2	640	628	620
3	634	620	618
4	632	615	616
5	628	610	610
6	622	605	606
7	615	600	600
8	610	596	594
9	606	590	590
10	592	512	508
11	514	486	483
12	485	471	470
13	475	467	462
14	466	462	458
15	461	456	446

(Contd.)

FIGURE NO. 9A

POTENTIOMETRIC TITRATIONS

DL-VALINE-$CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M DL-VALINE (FROM BURETTE)

B = 10 ml OF 0·005 M $CrCl_2$ Vs. 20 ml OF 0·05 M DL-VALINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M DL-VALINE (FROM BURETTE)

VIDE TABLE NO. 9A

1	2	3	4
16	455	452	438
17	450	447	434
18	440	442	430
19	435	439	418
20	432	430	412

1st. titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M DL-Valine (from burette).

2nd. titration :- 10 ml of 0.05M Chromium(II) Chloride ageinst 20 ml of 0.05M DL-Valine (from burette).

3rd. titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M DL-Valine (from burette).

(Vide Fig. No.9 A)

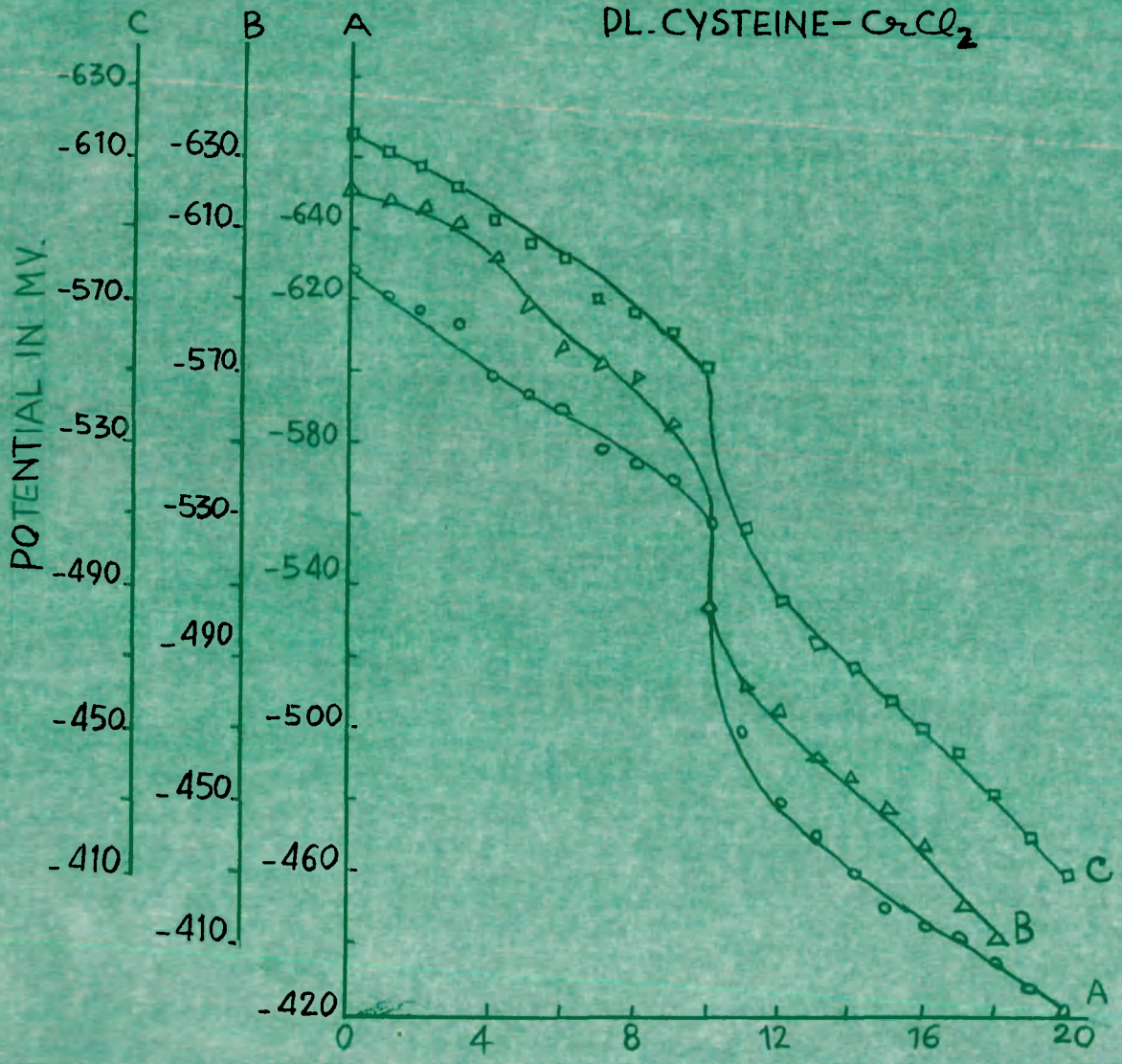
T A B L E No.10 A

Potentiometric titrations of Chromium(II) Chloride against DL-Cysteine

Vol.of DL-Cysteine added.(ml)	1st.Titration. A	2nd.Titration. B	3rd.Titration. C
1	2	3	4
	Potential in mv		
0	-628	620	-616
1	622	618	612
2	618	615	608
3	614	610	602
4	599	600	592
5	594	592	586
6	590	588	582
7	578	576	570
8	575	572	566
9	570	568	560
10	558	555	552
11	500	505	509
12	480	482	486
13	472	476	476

(Contd.)

FIGURE NO. 10 A
POTENTIOMETRIC TITRATIONS.
DL-CYSTEINE- $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M DL-CYSTEINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M DL-CYSTEINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M DL-CYSTEINE (FROM BURETTE)

VIDE TABLE NO. 10A

1	2	3	4
14.	460	462	468
15	450	456	458
16	446	448	450
17	442	438	444
18	436	420	432
19	428	416	420
20	421	412	410

1st. titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M DL-Cysteine (from burette).

2nd. titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M DL-Cysteine (from burette).

3rd. titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M DL-Cysteine (from burette).

(Vide Fig. No.10 A)

T A B L E No.11 A

Potentiometric titrations of Chromium(II) Chloride against DL-Methionine

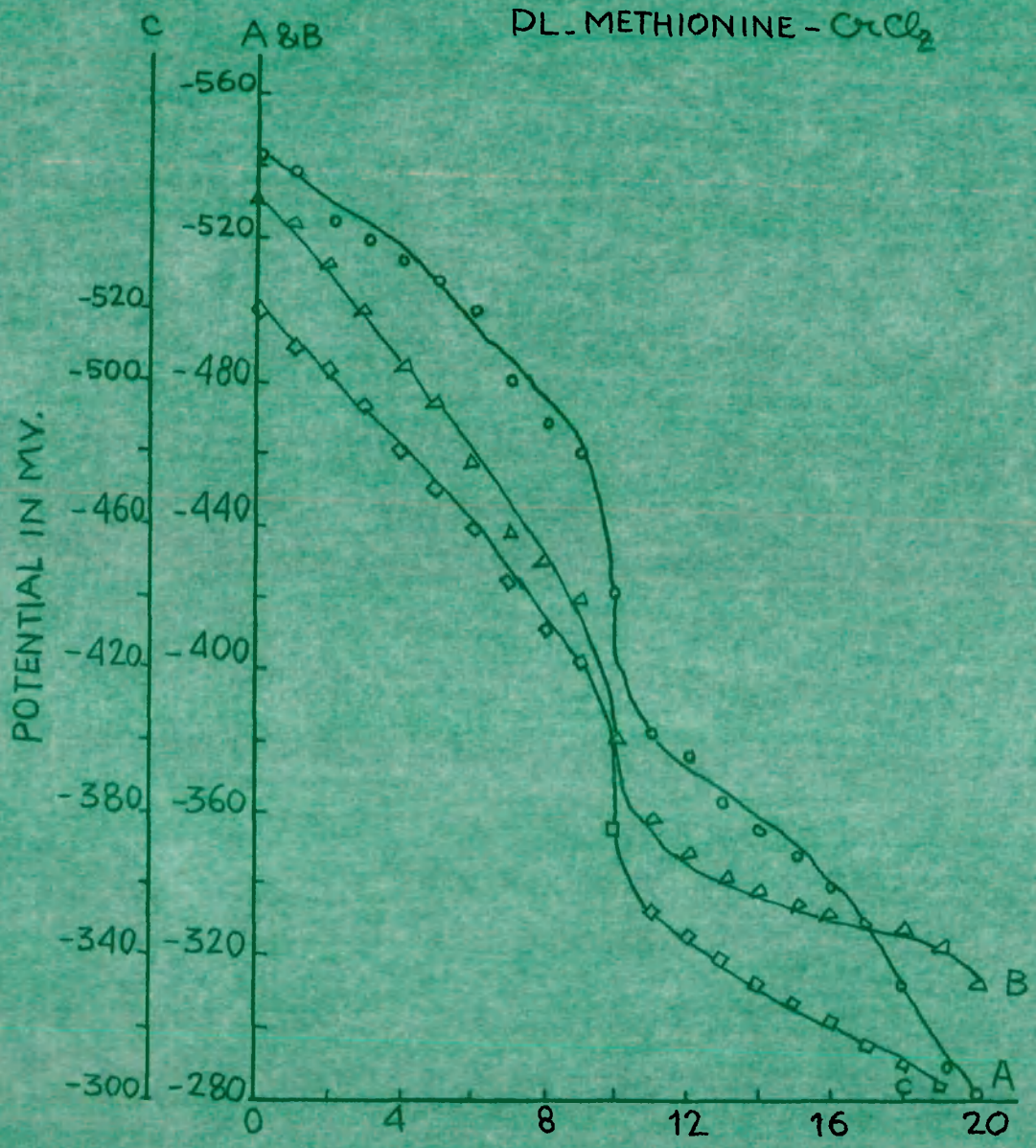
Vol. of DL-Methionine added. (ml)	1st. Titration. A	2nd. Titration. B	3rd. Titration. C
	Potential in mv		
0	-542	-530	-520
1	538	524	510
2	424	512	504
3	520	500	494
4	514	484	480
5	508	474	470
6	500	458	460
7	480	438	444
8	468	430	430
9	460	420	422
10	421	380	376
11	382	358	352
12	376	348	346
13	363	342	340

(Contd.)

FIGURE NO. 11A

POTENTIOMETRIC TITRATIONS.

DL-METHIONINE - $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M DL-METHIONININE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M DL-METHIONINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M DL-METHIONINE (FROM BURETTE)

VIDE TABLE NO. 11A

1	2	3	4
14	356	338	334
15	348	334	330
16	340	332	328
17	330	330	322
18	312	328	316
19	286	322	310
20	280	312	308

1st. titration:- 10 ml. of 0.066M Chromium(II) Chloride against 20 ml of 0.066M DL-Methionine (from burette).

2nd. titration:- 10 ml. of 0.05M Chromium(II) Chloride against 20 ml of 0.05M DL-Methionine (from burette).

3rd. titration:- 10 ml. of 0.04M Chromium(II) Chloride against 20 ml. of 0.04M DL-Methionine (from burette).

(Vide Fig. No.11 A)

T A B L E No.12 A

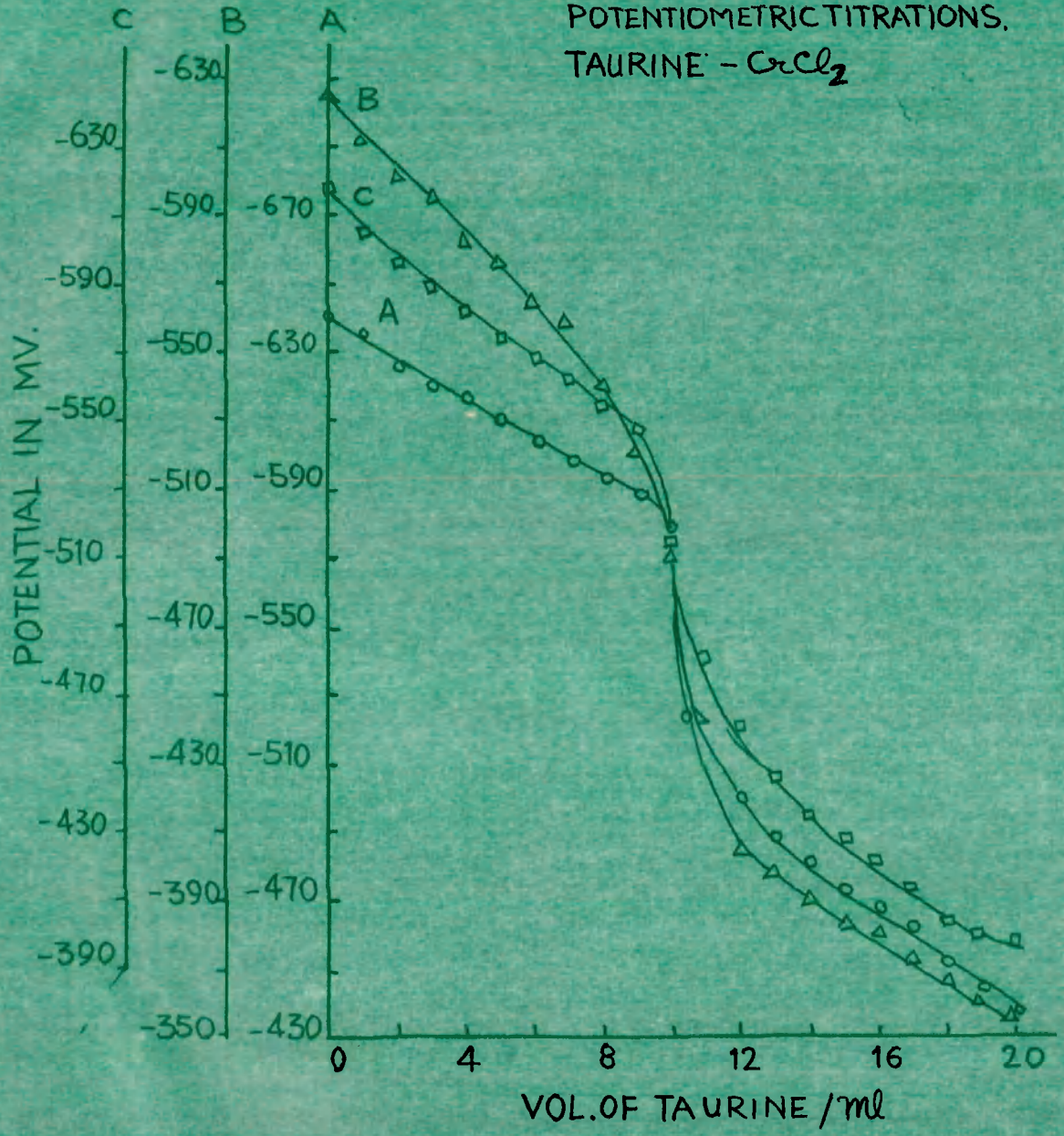
Potentiometric titrations of Chromium(II) Chloride against Taurine

Vol.of Taurine added. (ml)	1st.Titration. A	2nd.Titration. B	3rd.Titration. C
1	2	3	4
	Potential in mv		
0	-640	-625	-618
1	636	612	605
2	626	600	596
3	621	596	590
4	618	592	582
5	610	582	574
6	604	576	568
7	598	565	562
8	592	560	556
9	588	520	546
10	578	490	506
11	524	434	480
12	498	404	460
13	488	398	445

(Contd.)

FIGURE NO. 12 A

POTENTIOMETRIC TITRATIONS.
TAURINE - $CrCl_2$



A = 10 ml OF 0·066 M $CrCl_2$ Vs. 20 ml OF 0·066 M TAURINE (FROM BURETTE)

B = 10 ml OF 0·05 M $CrCl_2$ Vs. 20 ml OF 0·05 M TAURINE (FROM BURETTE)

C = 10 ml OF 0·04 M $CrCl_2$ Vs. 20 ml OF 0·04 M TAURINE (FROM BURETTE)

VIDE TABLE NO. 12 A

1	2	3	4
14	480	390	434
15	472	384	428
16	468	380	420
17	462	372	412
18	450	366	402
19	442	362	400
20	436	356	398

1st.titration :- 10 ml of 0.066M Chromium(II) Chloride against 20 ml of 0.066M Taurine (from burette).

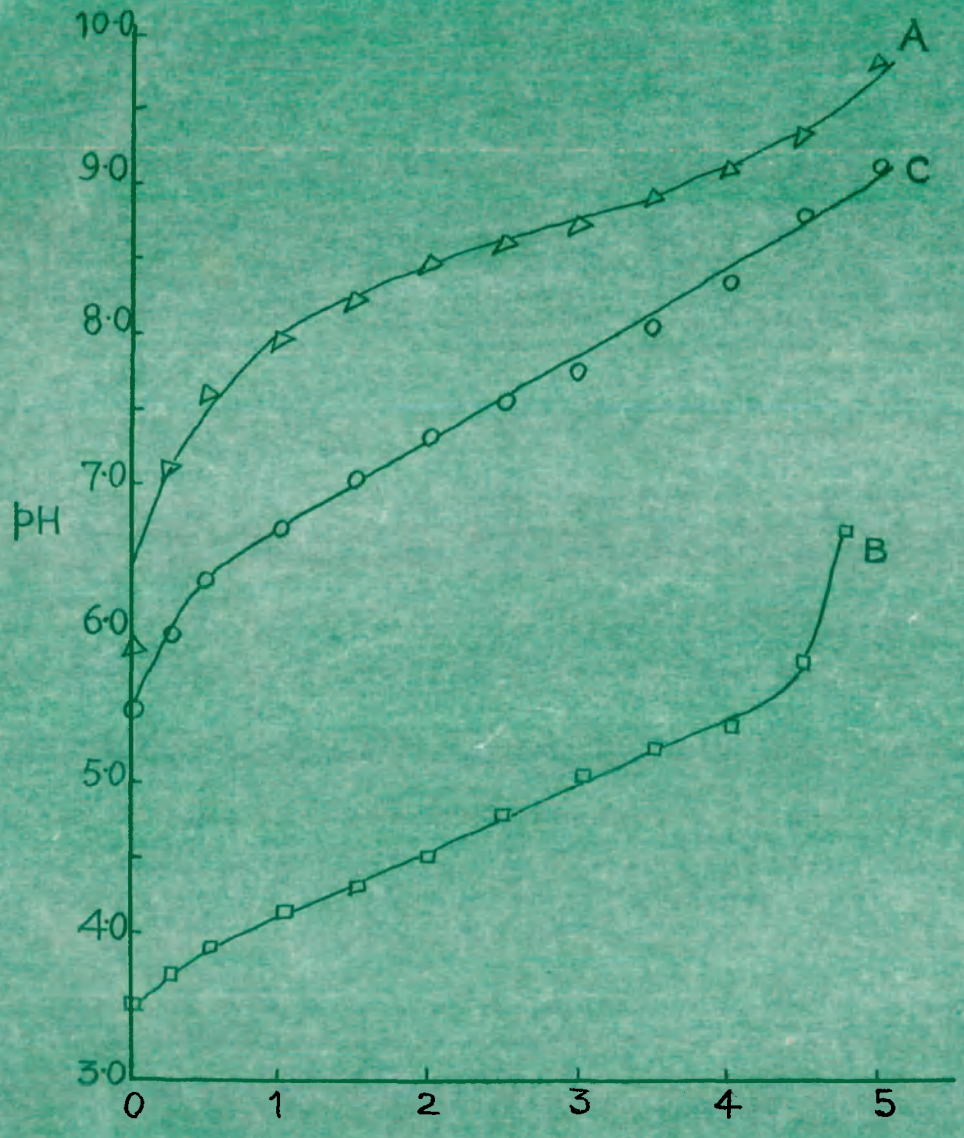
2nd.titration :- 10 ml of 0.05M Chromium(II) Chloride against 20 ml of 0.05M Taurine (from burette).

3rd.titration :- 10 ml of 0.04M Chromium(II) Chloride against 20 ml of 0.04M Taurine (from burette).

(Vide Fig. No.12 A)

FIGURE No. 2B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01ML - ASPARAGINE (IN THE CELL)

B = 50 ml OF 0·005 M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02ML - ASPARAGINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE No. 2B

T A B L E No.2 B

pH-metric titrations of Cr(II) L-Asparagine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	3.50	5.50
0.25	7.10	3.70	6.00
0.50	7.60	3.90	6.35
1.00	8.00	4.15	6.70
1.50	8.25	4.30	7.05
2.00	8.50	4.50	7.35
2.50	8.60	4.80	7.55
3.00	8.70	5.05	7.75
3.50	8.90	5.20	8.05
4.00	9.10	5.35	8.35
4.50	9.30	5.80	8.80
5.00	9.80	6.70	9.15

(A) = 50 ml of 0.01M L-Asparagine (in the cell)

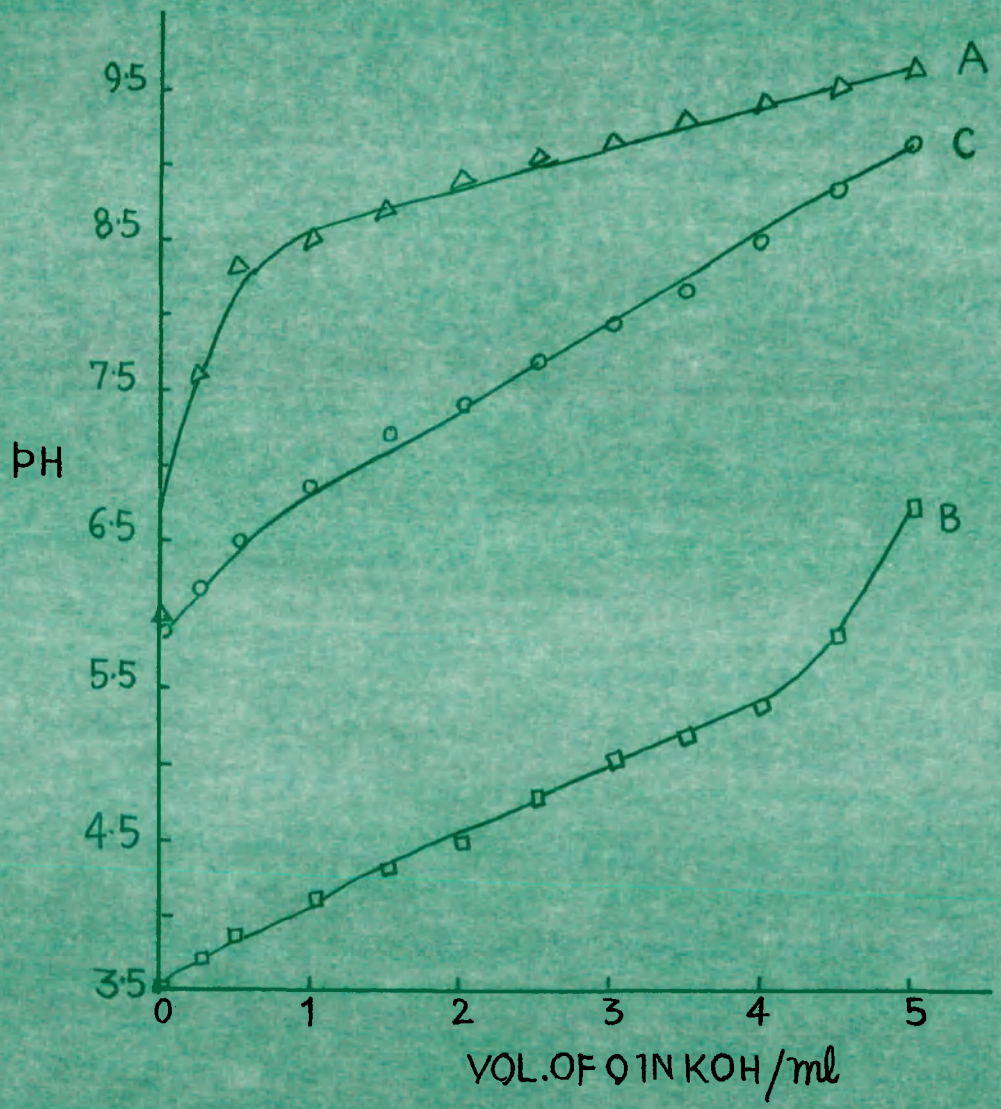
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M L-Asparagine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.2 B)

FIGURE NO. 3B

pH-METRIC TITRATIONS.



A = 50 ml OF 0·01M DL-α-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M DL-α-ALANINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 3B

T A B L E No.3 B

pH-metric titrations of Cr(II)-DL-α-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	3.50	5.90
0.25	7.60	3.70	6.15
0.50	8.30	3.90	6.50
1.00	8.50	4.15	6.85
1.50	8.70	4.30	7.20
2.00	8.90	4.50	7.40
2.50	9.05	4.80	7.70
3.00	9.15	5.05	7.95
3.50	9.30	5.20	8.15
4.00	9.40	5.35	8.50
4.50	9.50	5.85	8.85
5.00	9.60	6.70	9.15

(A) = 50 ml of 0.01M DL-α-Alanine (in the cell)

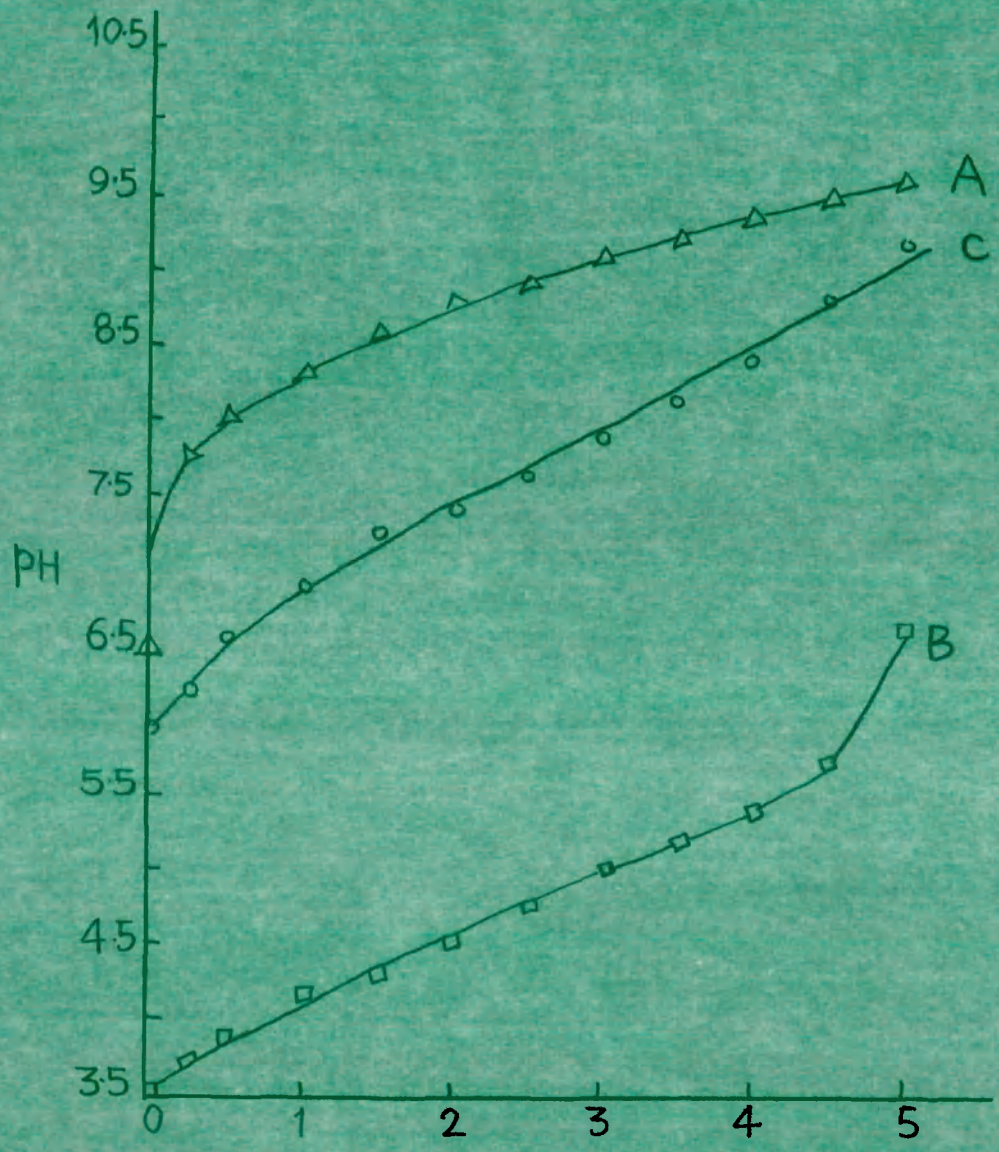
(B) = 50 ml of 0.005M Chromium Chloride(in the cell)

(C) = 25 ml of 0.02M DL-α-Alanine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.3 B)

FIGURE NO. 4B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M β-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M β-ALANINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 4B

TABLE No.4 B

pH-metric titrations of Cr(II)-β-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.50	5.95
0.25	7.75	3.70	6.20
0.50	8.00	3.90	6.55
1.00	8.30	4.20	6.90
1.50	8.60	4.30	7.25
2.00	8.80	4.50	7.40
2.50	8.90	4.75	7.65
3.00	9.10	5.00	7.90
3.50	9.20	5.20	8.10
4.00	9.35	5.40	8.40
4.50	9.50	5.75	8.80
5.00	9.65	6.60	9.20

(A) = 50 ml of 0.01M β-Alanine (in the cell)

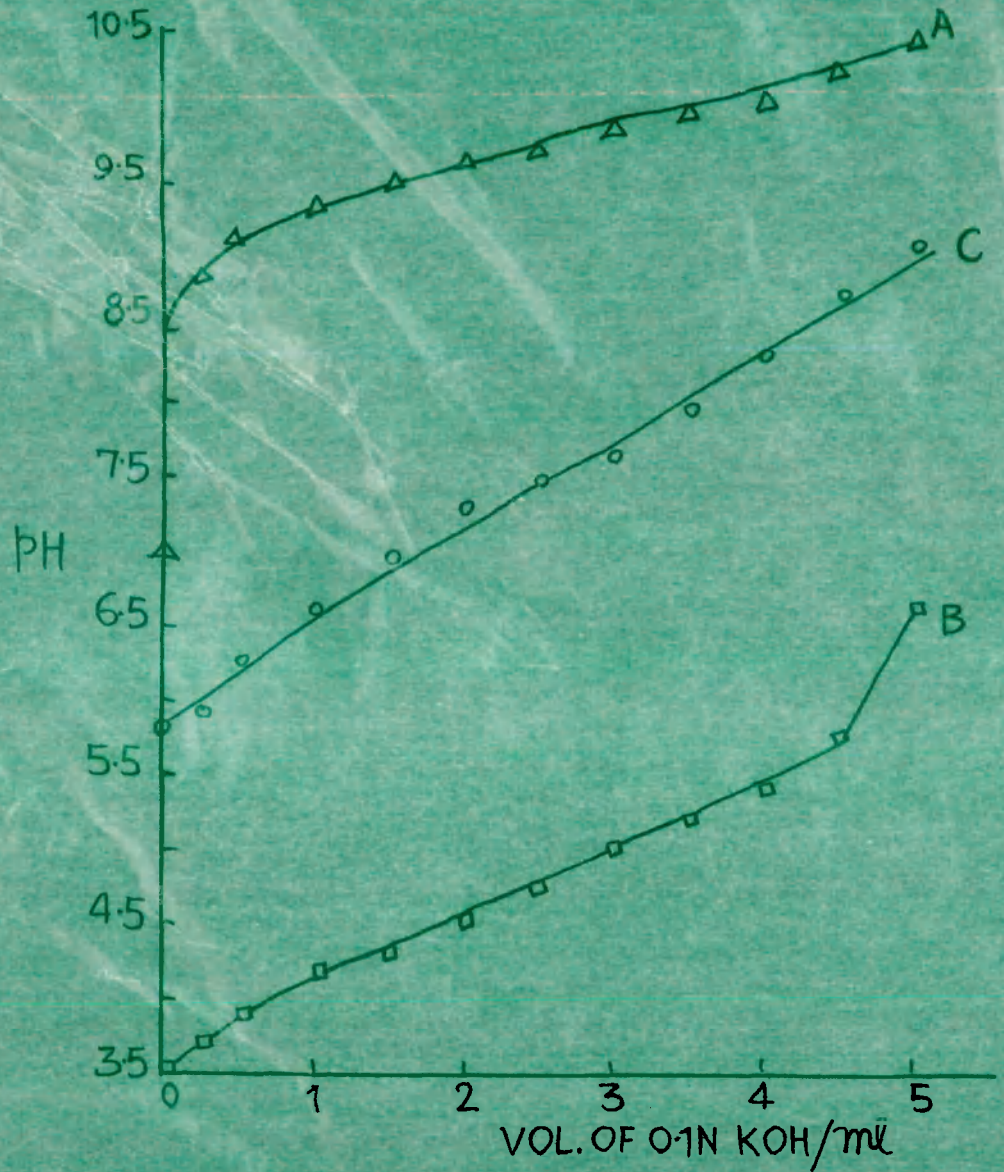
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M β-Alanine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.4 B)

FIGURE NO. 5B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01 M GLYCINE (IN THE CELL)

B = 50 ml OF 0·005 M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02 M GLYCINE + 25 ml OF 0·01 M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 5B

T A B L E No.5 B

pH-metric titrations of Cr(II)-Glycine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.50	5.80
0.25	8.80	3.70	5.90
0.50	9.10	3.90	6.25
1.00	9.30	4.20	6.60
1.50	9.50	4.30	6.95
2.00	9.60	4.50	7.25
2.50	9.70	4.75	7.45
3.00	9.80	5.00	7.65
3.50	9.90	5.20	7.95
4.00	10.00	5.40	8.25
4.50	10.20	5.75	8.70
5.00	10.40	6.60	9.05

(A) = 50 ml of 0.01M Glycine (in the cell)

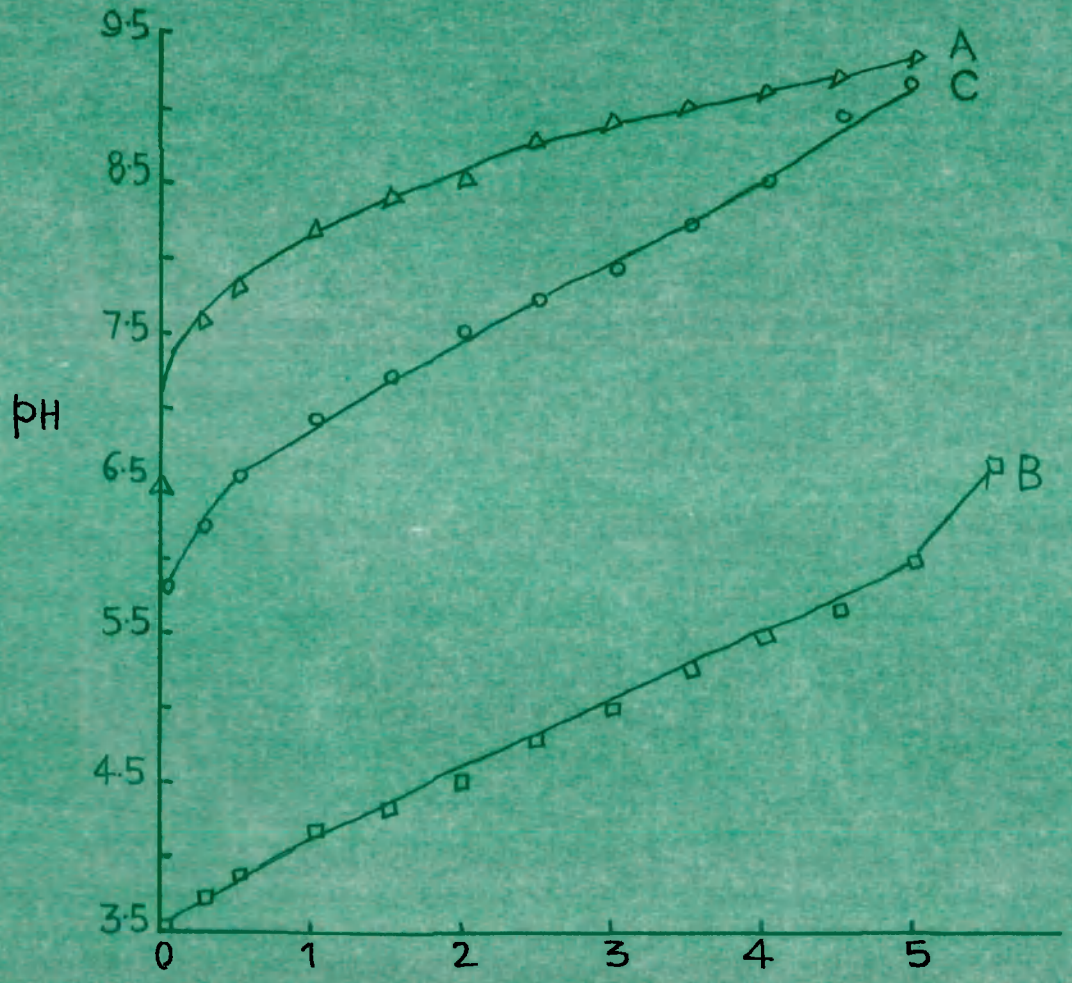
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M Glycine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.5 B)

FIGURE NO.6B

pH-METRIC TITRATIONS



VOL. OF 0·1N KOH / ml

A = 50 ml OF 0·01M DL-LEUCINE (IN THE CELL)

B = 50 ml OF 0·005 M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02 M DL-LEUCINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO.6B

T A B L E No.6 B

pH-metric titrations of Cr(II)-DL-Leucine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.50	5.80
0.25	7.60	3.70	6.20
0.50	7.80	3.90	6.55
1.00	8.20	4.20	6.90
1.50	8.40	4.30	7.20
2.00	8.50	4.50	7.50
2.50	8.80	4.75	7.70
3.00	8.90	5.00	7.90
3.50	9.00	5.20	8.20
4.00	9.10	5.40	8.50
4.50	9.20	5.75	8.95
5.00	9.35	6.60	9.15

(A) = 50 ml of 0.01M DL-Leucine (in the cell)

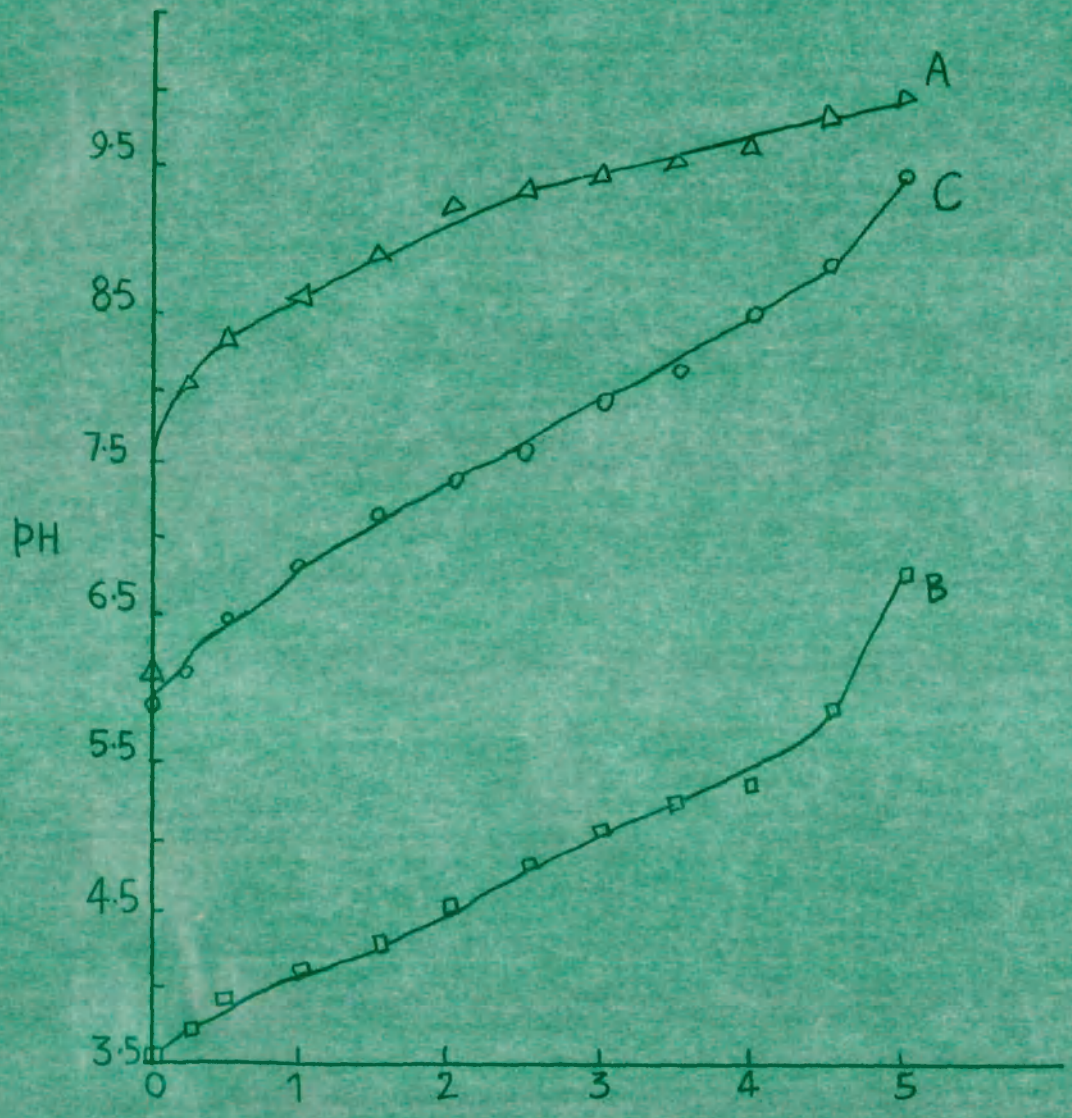
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M DL-Leucine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.6 B)

FIGURE NO. 7B

PH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-PROLINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M L. PROLINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 7B

T A B L E No.7 B

pH-metric titrations of Cr(II)- L-Proline system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.10	3.50	5.90
0.25	8.00	3.70	6.10
0.50	8.30	3.90	6.45
1.00	8.60	4.15	6.80
1.5	8.90	4.30	7.15
2.00	9.20	4.50	7.35
2.50	9.30	4.80	7.65
3.00	9.40	5.05	7.90
3.50	9.50	5.20	8.10
4.00	9.60	5.35	9.45
4.50	9.80	5.80	8.80
5.00	9.90	6.70	9.40

(A) = 50 ml of 0.01M L-Proline (in the cell)

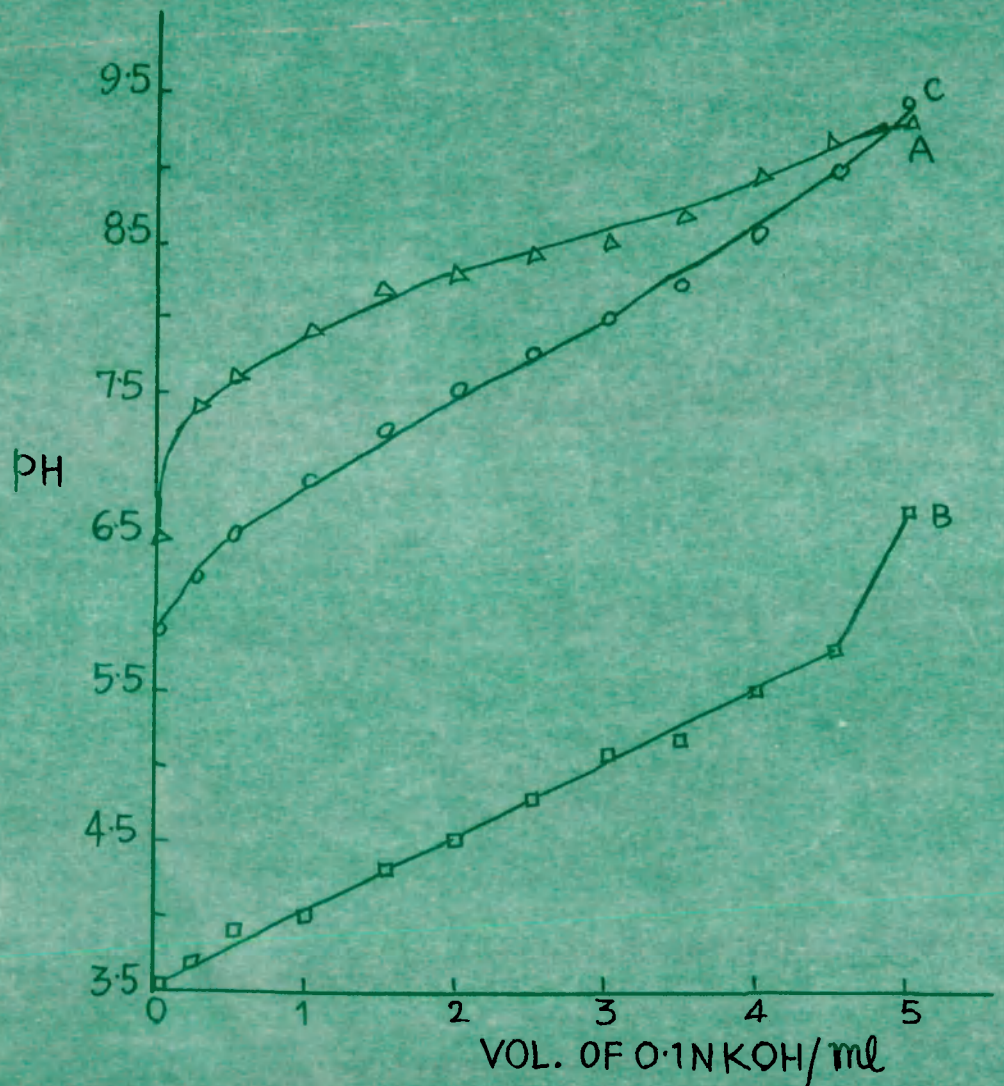
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M L-Proline + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.7 B)

FIGURE NO. 8B

pH-METRIC TITRATIONS.



A = 50 ml OF 0·01M DL-SERINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M DL-SERINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 8B

T A B L E No.8 B

pH-metric titrations of Cr(II)-DL-Serine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.50	5.90
0.25	7.40	3.70	6.25
0.50	7.60	3.90	6.55
1.00	7.90	4.00	6.90
1.50	8.20	4.30	7.25
2.00	8.30	4.50	7.50
2.50	8.40	4.80	7.75
3.00	8.50	5.10	8.00
3.50	8.70	5.20	8.25
4.00	8.95	5.50	8.55
4.50	9.20	5.80	9.00
5.00	9.30	6.70	9.45

(A) = 50 ml of 0.01M DL-Serine (in the cell)

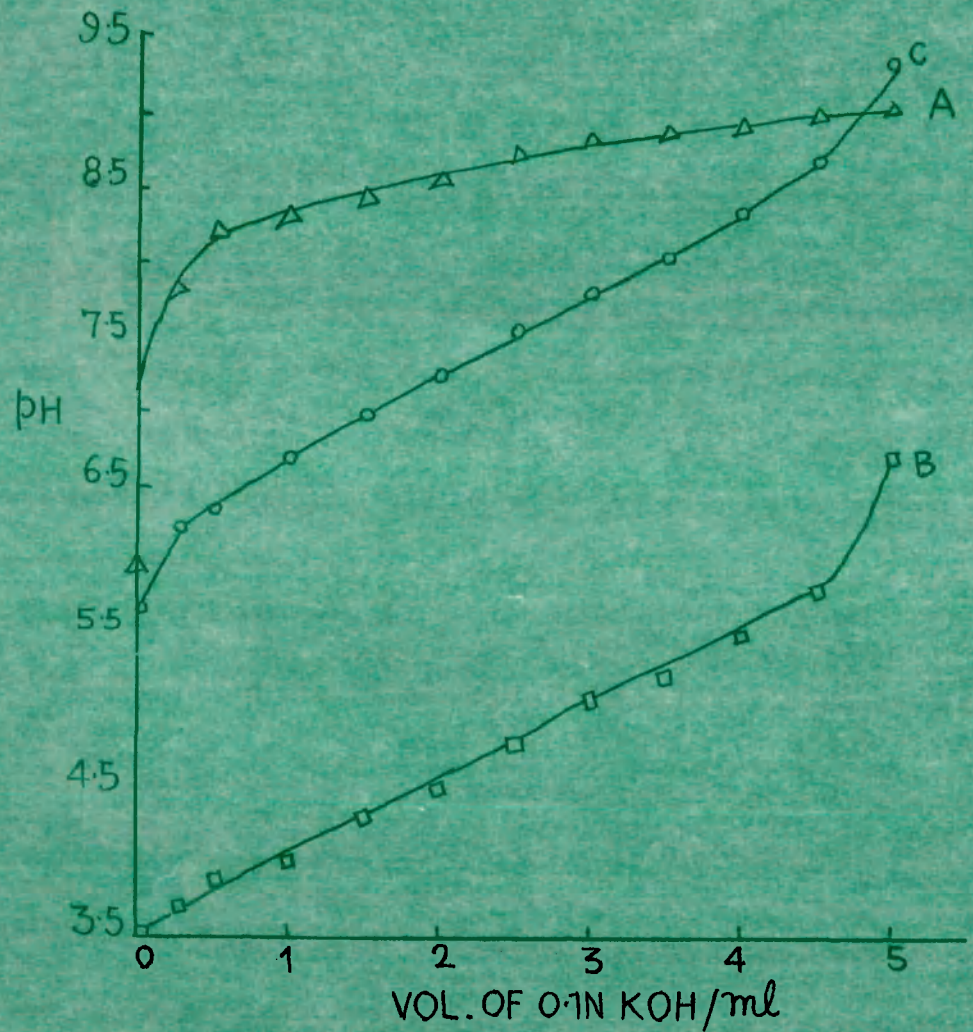
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M DL-Serine + 25 ml of 0.01M Chromium(II) Chloride(in the cell)

(Vide Fig. No.8 B)

FIGURE No.9B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL-VALINE (IN THE CELL)

B = 50 ml OF 0·005 M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M DL-VALINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE No.9B

T A B L E No.9 B

pH-metric titrations of Cr(II)-DL-Valine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	3.50	5.70
0.25	7.60	3.70	6.25
0.50	7.95	3.90	6.35
1.00	8.05	4.00	6.70
1.50	8.20	4.30	7.05
2.00	8.30	4.50	7.25
2.50	8.50	4.80	7.55
3.00	8.60	5.10	7.80
3.50	8.70	5.20	8.00
4.00	8.80	5.50	8.35
4.50	8.95	5.80	8.70
5.00	9.05	6.70	9.35

(A) = 50 ml of 0.01M DL-Valine (in the cell)

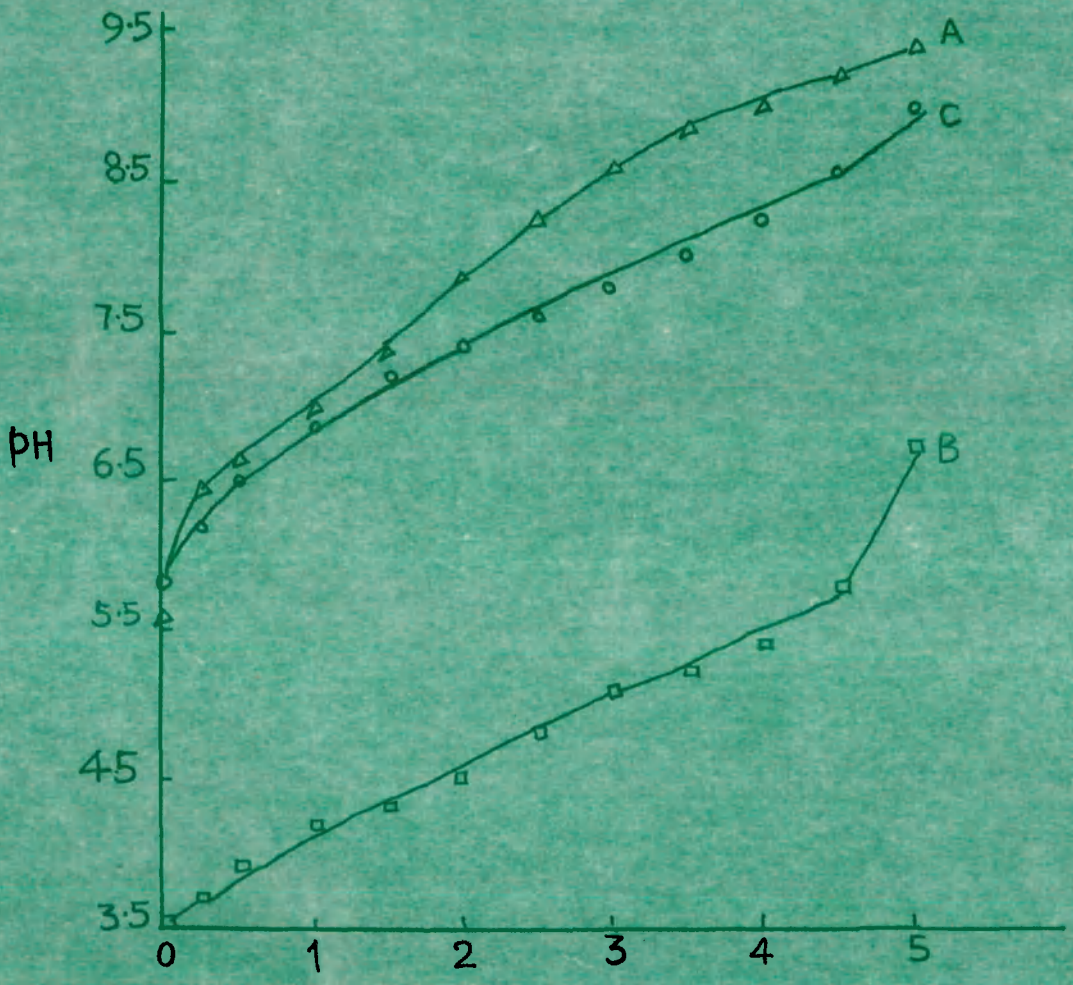
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M DL-Valine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.9 B)

FIGURE NO. **10B**

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M CYSTEINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M CYSTEINE + 25 ml OF 0·02M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. **10B**

TABLE No.10 B

pH-metric titrations of Cr(II)-Cysteine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.60	3.56	5.80
0.25	6.45	3.70	6.20
0.50	6.65	3.90	6.55
1.00	6.95	4.20	6.90
1.50	7.35	4.30	7.20
2.00	7.85	4.50	7.40
2.50	8.25	4.80	7.60
3.00	8.55	5.10	7.75
3.50	8.85	5.20	8.00
4.00	9.00	5.40	8.20
4.50	9.20	5.80	8.55
5.00	9.40	6.70	9.00

(A) = 50 ml of 0.01M Cysteine (in the cell)

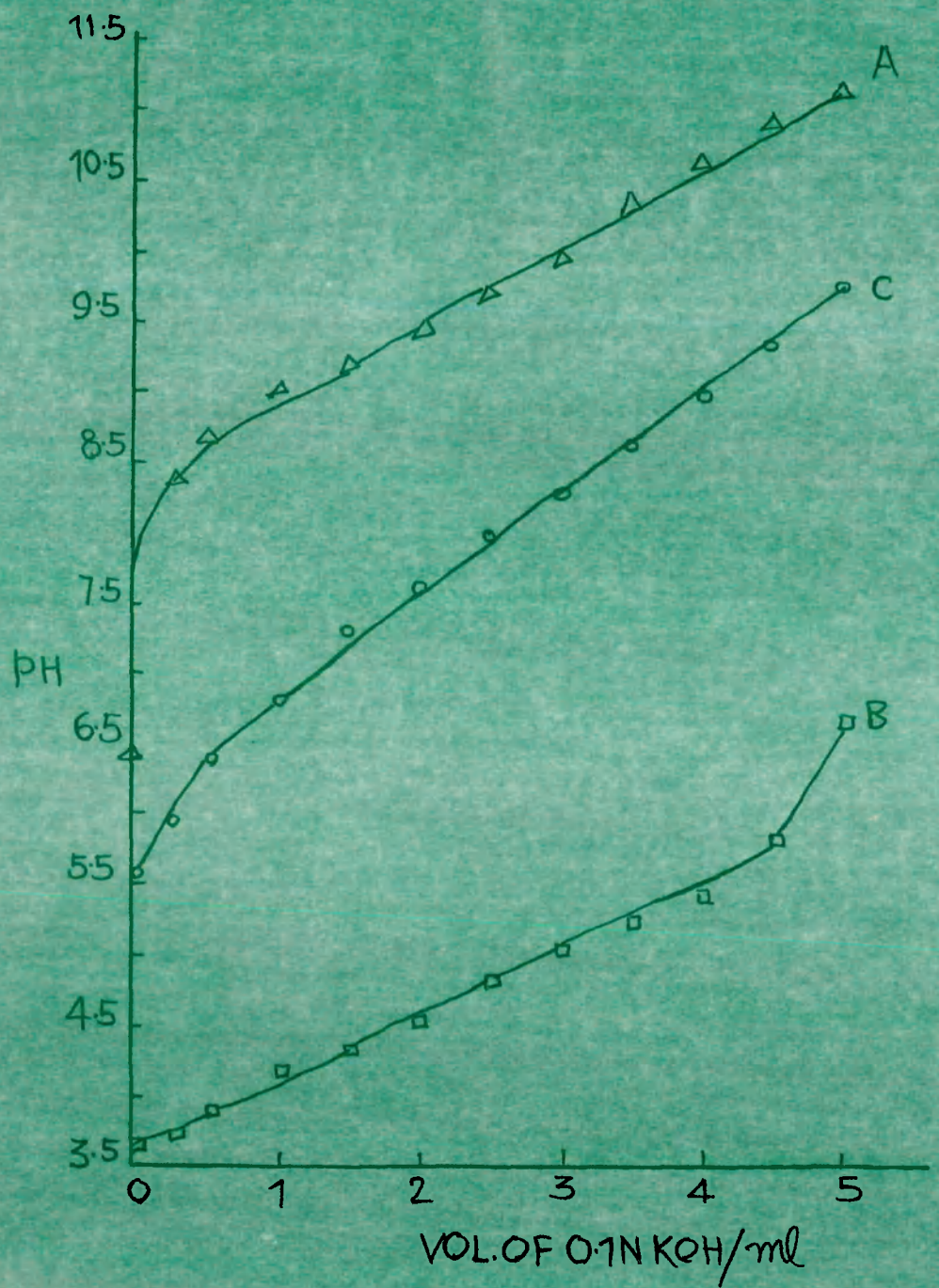
(B) = 50 ml of 0.005M Chromium Chloride (in the cell)

(C) = 25 ml of 0.02M Cysteine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.10 B)

FIGURE NO. 11B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL-METHIONINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M DL-METHIONINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO. 11B

T A B L E No.11 B

pH-metric titrations of Cr(II)-DL-Methionine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.40	3.56	5.65
0.25	8.40	3.70	5.95
0.50	8.70	3.90	6.40
1.00	9.00	4.20	6.80
1.50	9.20	4.30	7.30
2.00	9.40	4.50	7.65
2.50	9.70	4.80	7.95
3.00	9.90	5.05	8.25
3.50	10.30	5.20	8.65
4.00	10.60	5.40	8.95
4.50	10.90	5.80	9.30
5.00	11.10	6.65	9.70

(A) = 50 ml of 0.01M DL-Methionine (in the cell

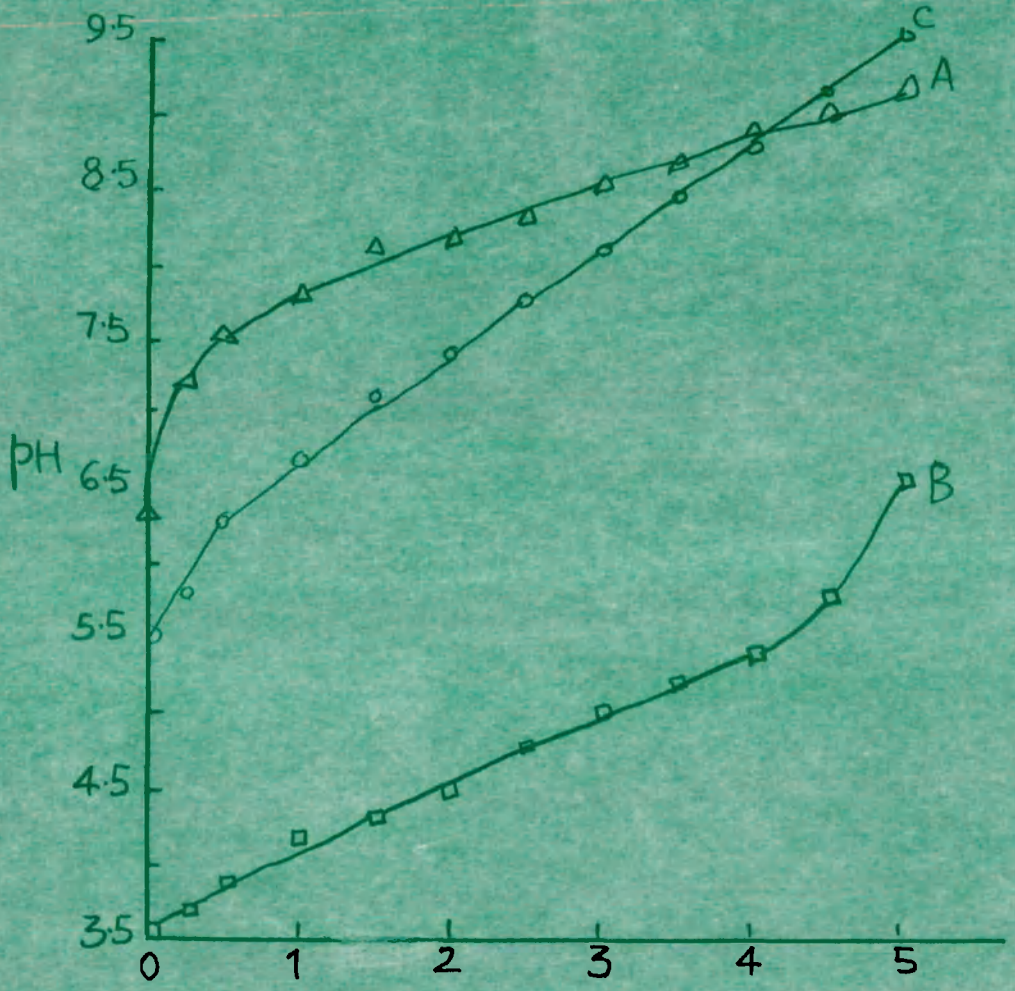
(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M DL-Methionine + 25 ml of 0.01M Chromium(II) Cloride (in the cell)

(Vide Fig. No.11 B)

FIGURE NO.12B

PH-METRIC TITRATIONS.



VOL. OF 0·1N KOH /ml

A = 50 ml OF 0·01M TAURINE (IN THE CELL)

B = 50 ml OF 0·005M $CrCl_2$ (IN THE CELL)

C = 25 ml OF 0·02M TAURINE + 25 ml OF 0·01M $CrCl_2$ (IN THE CELL)

VIDE TABLE NO.12B

TABLE No.12 B

pH-metric titrations of Cr(II)-Taurine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.35	3.56	5.55
0.25	7.25	3.70	5.80
0.50	7.55	3.90	6.30
1.00	7.80	4.20	6.70
1.50	8.15	4.30	7.15
2.00	8.20	4.50	7.45
2.50	8.35	4.80	7.80
3.00	8.55	5.05	8.10
3.50	8.70	5.20	8.50
4.00	8.90	5.40	8.85
4.50	9.10	5.80	9.20
5.00	9.20	6.65	9.55

(A) = 50 ml of 0.01M Taurine (in the cell)

(B) = 50 ml of 0.005M Chromium(II) Chloride (in the cell)

(C) = 25 ml of 0.02M Taurine + 25 ml of 0.01M Chromium(II) Chloride (in the cell)

(Vide Fig. No.12 B)

TABLE No.2 C

pH-metric titration of L - Asparagine (0.01M; pK_a = 8.85) and Chromium(II) Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.50	xx	xx	xx	xx
0.25	6.00	0.10	-4.8722	3.9153	xx
0.50	6.35	0.20	-4.5458	3.9385	xx
1.00	6.70	0.40	-4.2445	3.9839	xx
1.50	7.05	0.57	-3.9495	4.0445	xx
2.00	7.35	0.74	-3.7108	xx	xx
2.50	7.55	0.93	-3.5808	xx	xx
3.00	7.75	1.11	-3.4615	xx	xx
3.50	8.05	1.26	-3.2712	xx	3.0234
4.00	8.35	1.42	-3.0865	xx	3.0545
4.50	8.80	1.56	-2.7085	xx	2.9746
5.00	9.15	1.81	-2.7410	xx	xx

Mean log K' = 3.96

Mean log K" = 3.01

$\log K_s$ = 3.96 + 3.01 = 6.97 Calculated.

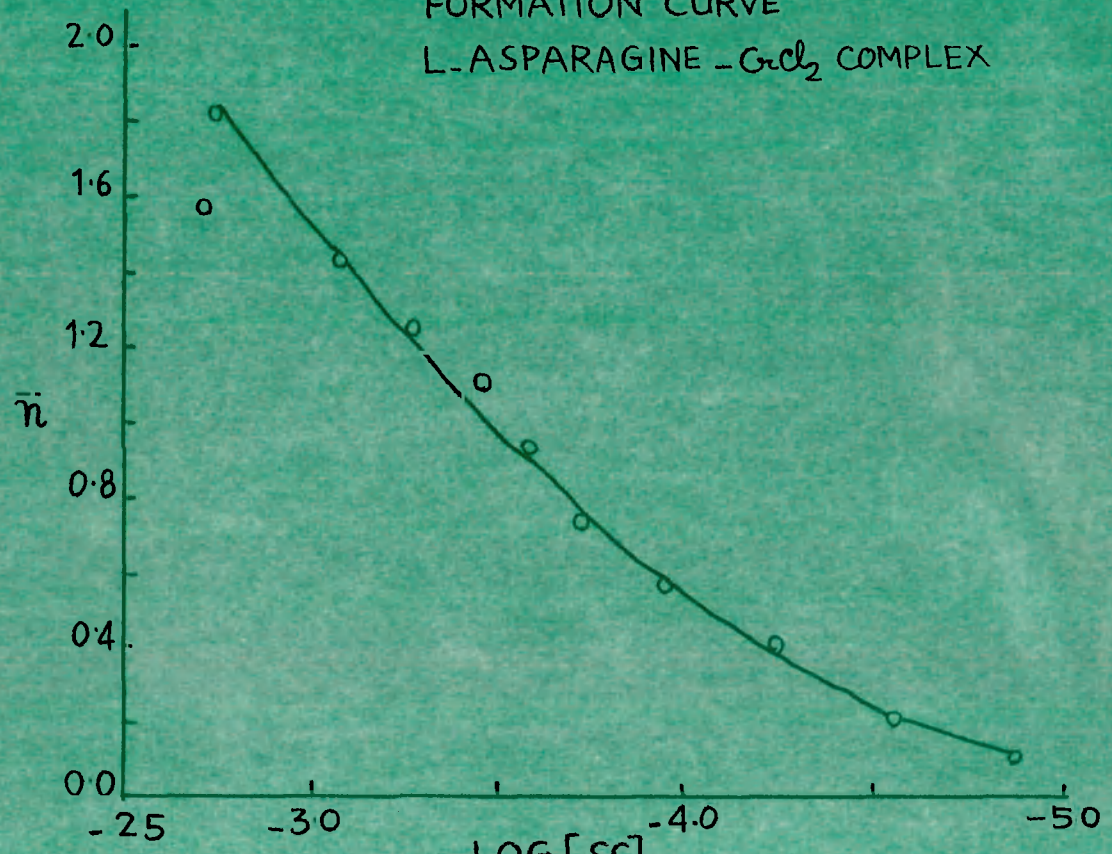
$\log K_s$ = 6.92 Graphically.

(Vide Fig. No.2 C)

FIGURE NO. 2C

FORMATION CURVE

L-ASPARAGINE - $CrCl_2$ COMPLEX

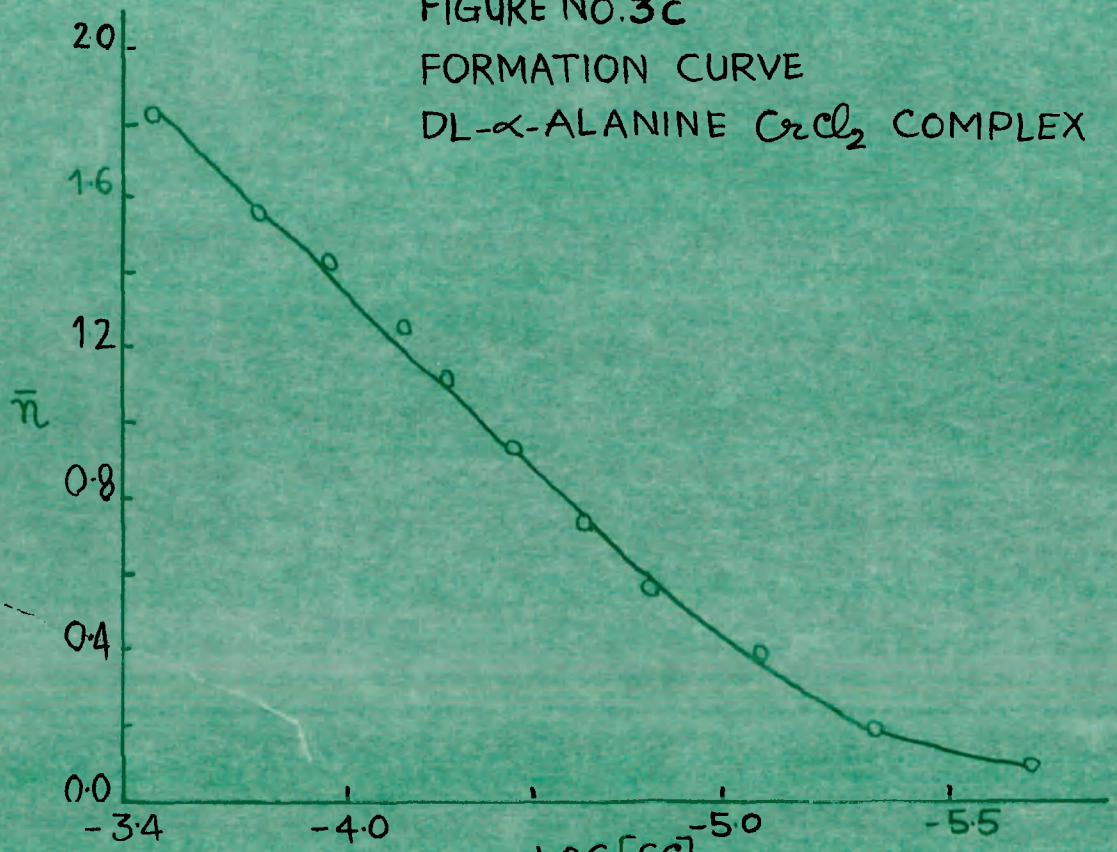


VIDE TABLE NO. 2C

FIGURE NO. 3C

FORMATION CURVE

DL-α-ALANINE $CrCl_2$ COMPLEX



VIDE TABLE NO. 3C

T A B L E No.3 C

pH-metric titration of DL-∝-Alanine (0.01M; pK_a = 9.86) and Chromium(II) Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.15	0.10	-5.7122	4.556	xx
0.50	6.50	0.20	-5.4058	4.7983	xx
1.00	6.85	0.40	-5.1045	4.9099	xx
1.50	7.20	0.57	-4.8095	4.9543	xx
2.00	7.40	0.74	-4.6307	xx	xx
2.50	7.70	0.93	-4.4407	xx	xx
3.00	7.95	1.11	-4.2715	xx	xx
3.50	8.15	1.26	-4.1712	xx	3.9770
4.00	8.50	1.42	-3.9555	xx	3.9235
4.50	8.85	1.56	-3.7685	xx	3.8754
5.00	9.45	1.81	-3.4510	xx	xx

Mean log K' = 4.84

Mean log K" = 3.92

$\log K_s$ = 4.84 + 3.92 = 8.76 Calculated.

$\log K_s$ = 8.72 Graphically.

(Vide Fig. No.3 C)

T A B L E No.4 C

pH-metric titration of β-Alanine (0.01M; pK_a = 9.87) and Chromium(II) Chloride(0.005M; all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.95	xx	xx	xx	xx
0.25	6.20	0.10	-6.2822	5.3256	xx
0.50	6.65	0.20	-5.8558	5.3483	xx
1.00	6.90	0.40	-5.5545	5.4308	xx
1.50	7.25	0.57	-5.2595	5.4947	xx
2.00	7.40	0.74	-5.1718	xx	xx
2.50	7.65	0.93	-4.9908	xx	xx
3.00	7.90	1.11	-4.8215	xx	xx
3.50	8.10	1.26	-4.7212	xx	4.5277
4.00	8.40	1.42	-4.5465	xx	4.5145
4.50	8.80	1.56	-4.3185	xx	4.4954
5.00	9.20	1.81	-4.2010	xx	xx

Mean log K' = 5.39

Mean log K" = 4.50

log K_s = 5.39 + 4.50 = 9.89 Calculated.

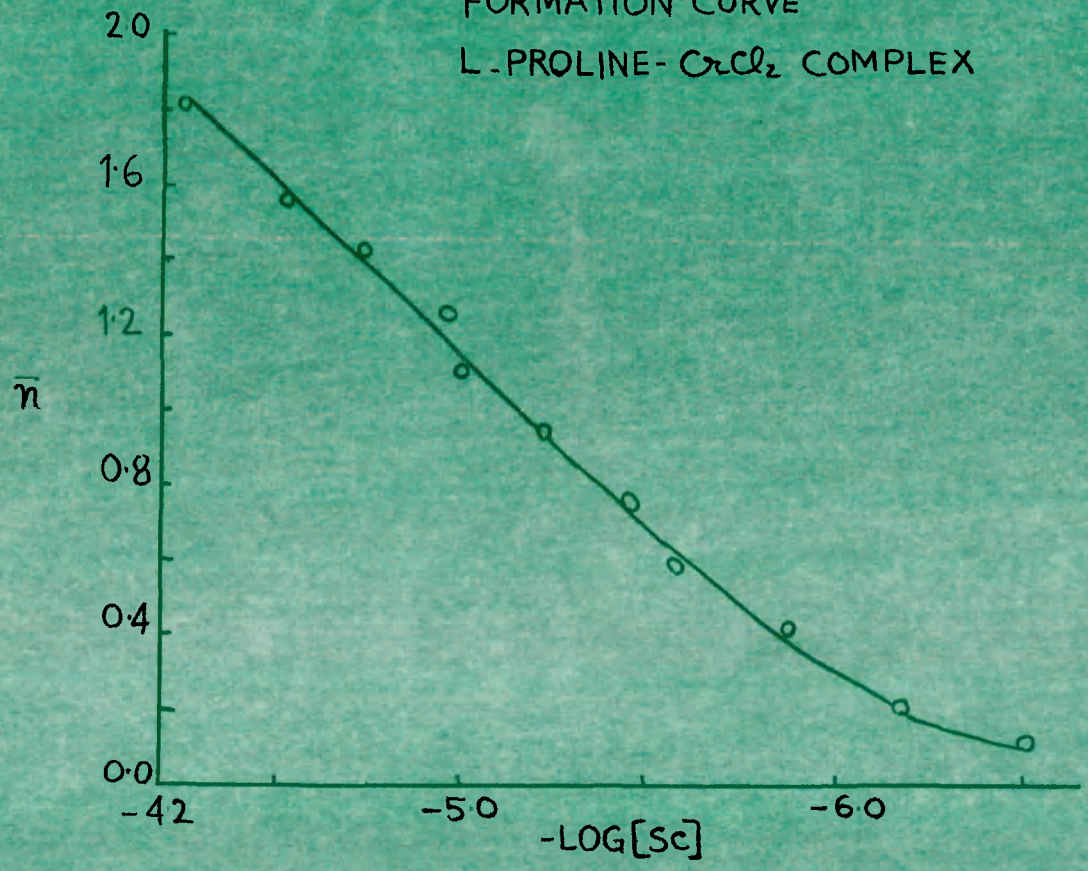
log K_s = 9.86 Grahically.

(Vide Fig. No.4 C)

FIGURE NO. 7C

FORMATION CURVE

L-PROLINE-$CrCl_2$ COMPLEX

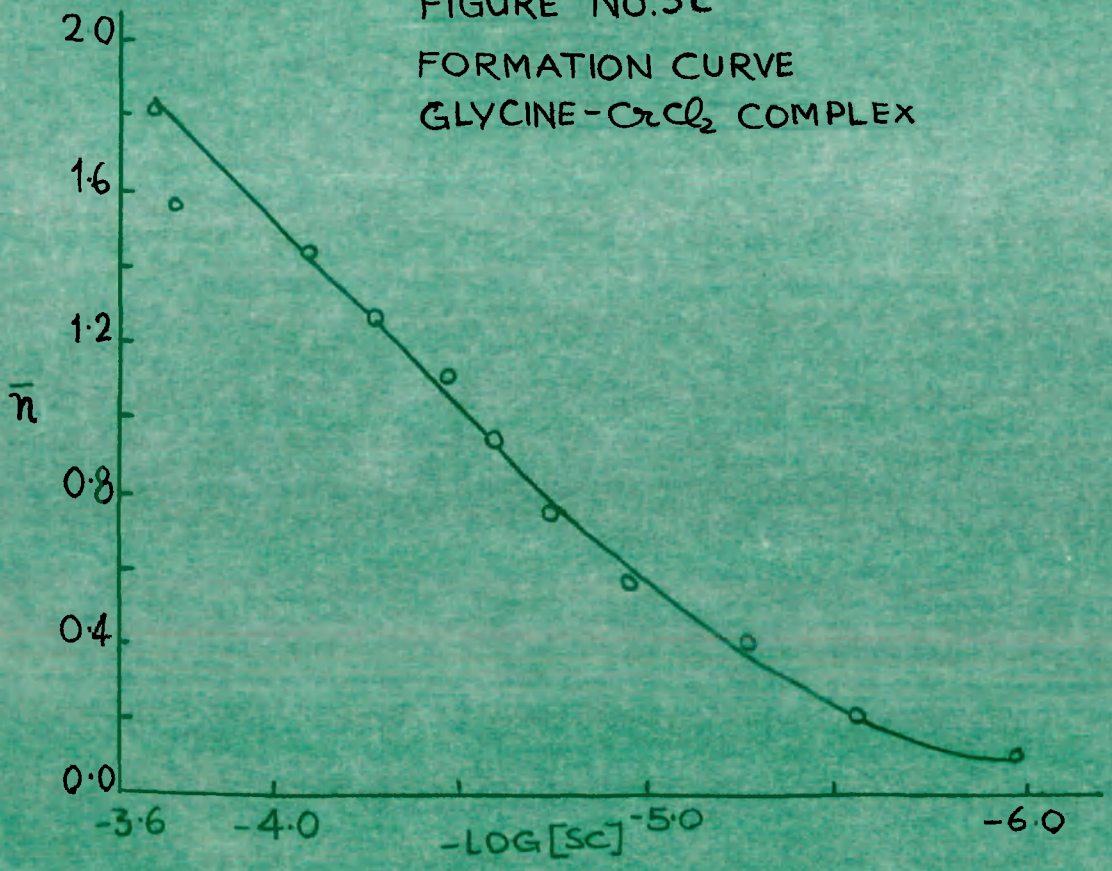


VIDE TABLE NO. 7C

FIGURE NO. 5C

FORMATION CURVE

GLYCINE-$CrCl_2$ COMPLEX



VIDE TABLE NO. 5C

T A B L E No.5 C

pH-metric titration of Glycine (0.01M; pK_a = 9.77) and Chromium(II) Chloride (0.005M; all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	5.90	0.10	-5.9022	4.9456	xx
0.50	6.25	0.20	-5.5668	4.9573	xx
1.00	6.60	0.40	-5.2645	5.0742	xx
1.50	6.90	0.57	-4.9695	5.1143	xx
2.00	7.25	0.74	-4.7608	xx	xx
2.50	7.45	0.93	-4.6008	xx	xx
3.00	7.65	1.11	-4.4815	xx	xx
3.50	7.95	1.26	-4.2812	xx	4.0877
4.00	8.25	1.42	-4.1065	xx	4.0745
4.50	8.70	1.56	-3.7285	xx	3.9354
5.00	9.05	1.81	-3.6618	xx	xx

Mean log K' = 5.02

Mean log K" = 4.03

$\log K_s$ = 5.02 + 4.03 = 9.05 Calculated.

$\log K_s$ = 9.02 Graphically.

(Vide Fig. No.5 C)

T A B L E No.6 C

pH-metric titration of DL-Leucine (0.01M; pK_a = 9.74) and Chromium(II) Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.20	0.10	-5.5622	4.6056	xx
0.50	6.55	0.20	-5.1358	4.6273	xx
1.00	6.90	0.40	-4.9345	4.6442	xx
1.50	7.20	0.57	-4.6895	4.6543	xx
2.00	7.50	0.74	-4.4508	xx	xx
2.50	7.70	0.93	-4.3208	xx	xx
3.00	7.90	1.11	-4.2015	xx	xx
3.50	8.20	1.26	-4.0012	xx	3.8077
4.00	8.50	1.42	-3.7265	xx	3.7945
4.50	8.95	1.56	-3.5485	xx	3.7964
5.00	9.15	1.81	-3.5310	xx	xx

Mean log K' = 4.63

Mean log K" = 3.79

$\log K_a$ = 4.63 + 3.79 = 8.42 Calculated

$\log K_a$ = 8.40 Graphically

(Vide Fig. No.6 C)

T A B L E No.7 C

pH-metric titration of L-Proline (0.01M; pK_a = 10.60) and Chromium(II) Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.10	0.10	-6.5222	5.5656	xx
0.50	6.45	0.20	-6.1958	5.5883	xx
1.00	6.80	0.40	-5.8945	5.7029	xx
1.50	7.15	0.57	-5.5995	5.7442	xx
2.00	7.35	0.74	-5.4608	xx	xx
2.50	7.65	0.93	-5.2308	xx	xx
3.00	7.90	1.11	-5.0015	xx	xx
3.50	8.10	1.26	-4.9612	xx	4.7677
4.00	8.45	1.42	-4.7365	xx	4.7045
4.50	8.80	1.56	-4.5585	xx	4.6664
5.00	9.40	1.81	-4.2410	xx	xx

Mean log K' = 5.64

Mean log K" = 4.71

$\log K_s$ = 5.64 + 4.71 = 10.35 Calculated.

$\log K_s$ = 10.32 Graphically.

(Vide Fig. No.7 C)

T A B L E No.8 C

pH-metric titration of DL-Serine (0.01M; pK_a = 9.15) and Chromium(II) Chloride(0.005M); all in 50 ml. $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.25	0.10	-4.9222	3.9657	xx
0.50	6.55	0.20	-4.6458	4.0384	xx
1.00	6.90	0.40	-4.3445	4.1522	xx
1.50	7.25	0.57	-4.0495	4.1943	xx
2.00	7.50	0.74	-3.8608	xx	xx
2.50	7.75	0.93	-3.6808	xx	xx
3.00	8.00	1.11	-3.5115	xx	xx
3.50	8.25	1.26	-3.3612	xx	3.1677
4.00	8.55	1.42	-3.1865	xx	3.1545
4.50	9.00	1.56	-2.9085	xx	3.0956
5.00	9.45	1.81	-2.7410	xx	xx

Mean log K' = 4.08

Mean log K" = 3.13

$\log K_s$ = 4.08 + 3.13 = 7.21 Calculated.

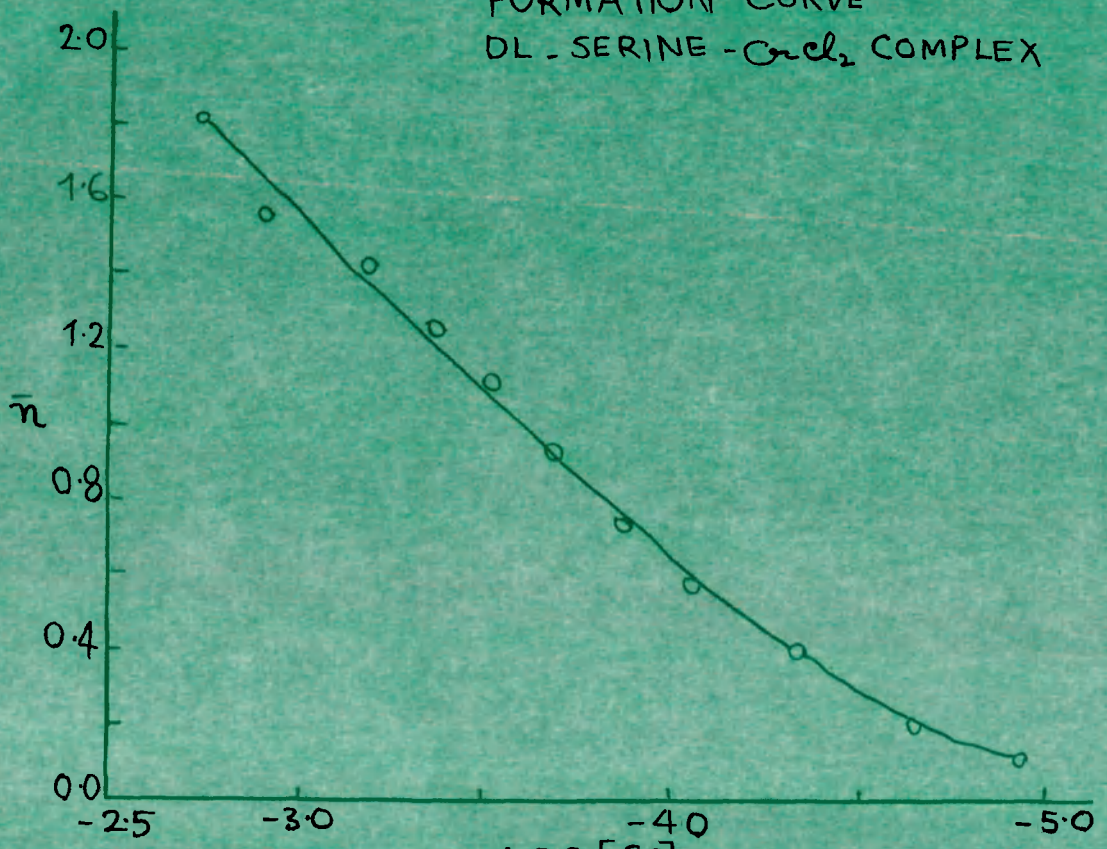
$\log K_s$ = 7.20 Graphically.

(Vide Fig. No.8 C)

FIGURE NO. 8C

FORMATION CURVE

DL - SERINE - $CrCl_2$ COMPLEX

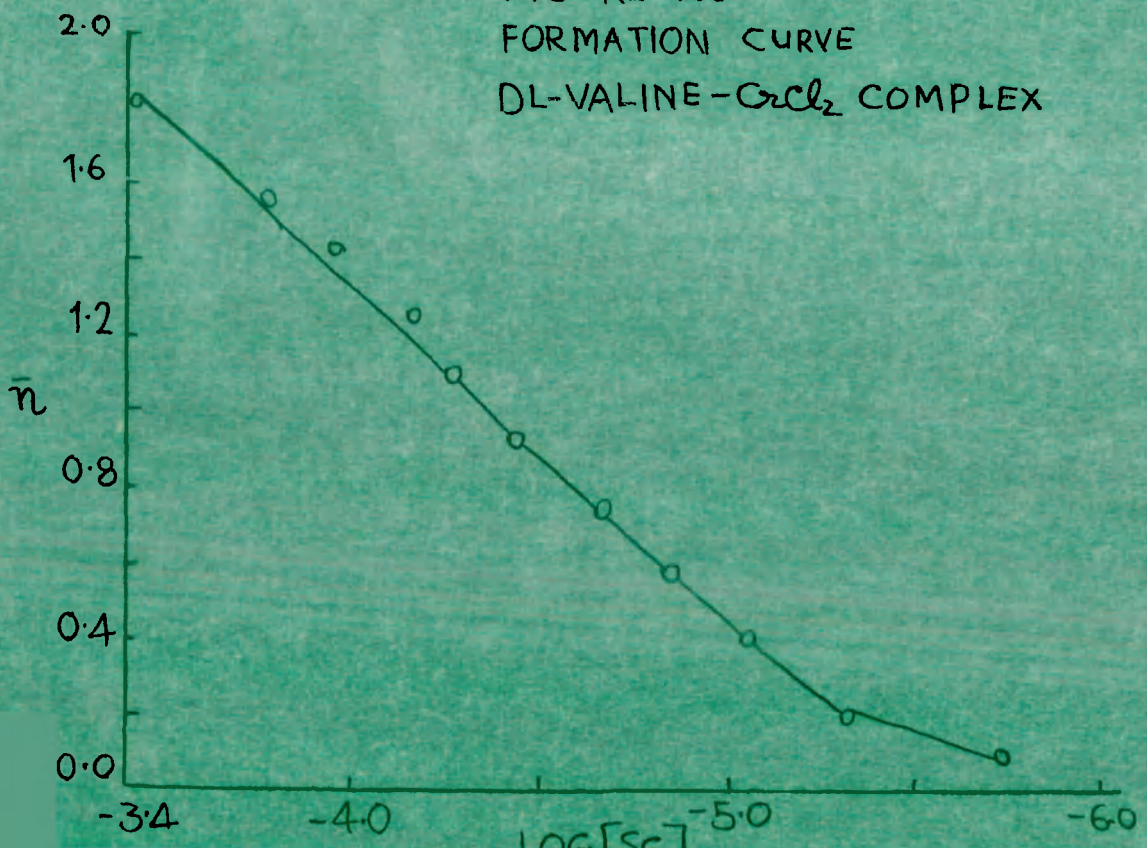


VIDE TABLE NO. 8C

FIGURE NO. 9C

FORMATION CURVE

DL-VALINE - $CrCl_2$ COMPLEX



VIDE TABLE NO. 9C

T A B L E No.9 C

pH-metric titration of DL-Valine (0.01M; pK_a = 9.71) and Chromium(II) Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.70	xx	xx	xx	xx
0.25	6.00	0.10	-5.7324	4.6715	xx
0.50	6.35	0.20	-5.3158	4.7083	xx
1.00	6.70	0.40	-5.0560	4.7100	xx
1.50	7.05	0.57	-4.8545	4.9900	xx
2.00	7.25	0.74	-4.6708	xx	xx
2.50	7.55	0.93	-4.4387	xx	xx
3.00	7.80	1.11	-4.2714	xx	xx
3.50	8.00	1.26	-4.1712	xx	3.9712
4.00	8.35	1.42	-3.9568	xx	3.9231
4.50	8.70	1.56	-3.7686	xx	3.8710
5.00	9.35	1.81	-3.4010	xx	xx

Mean log K' = 4.76

Mean log K" = 3.92

$\log K_s$ = 4.76 + 3.92 = 8.68 Calculated

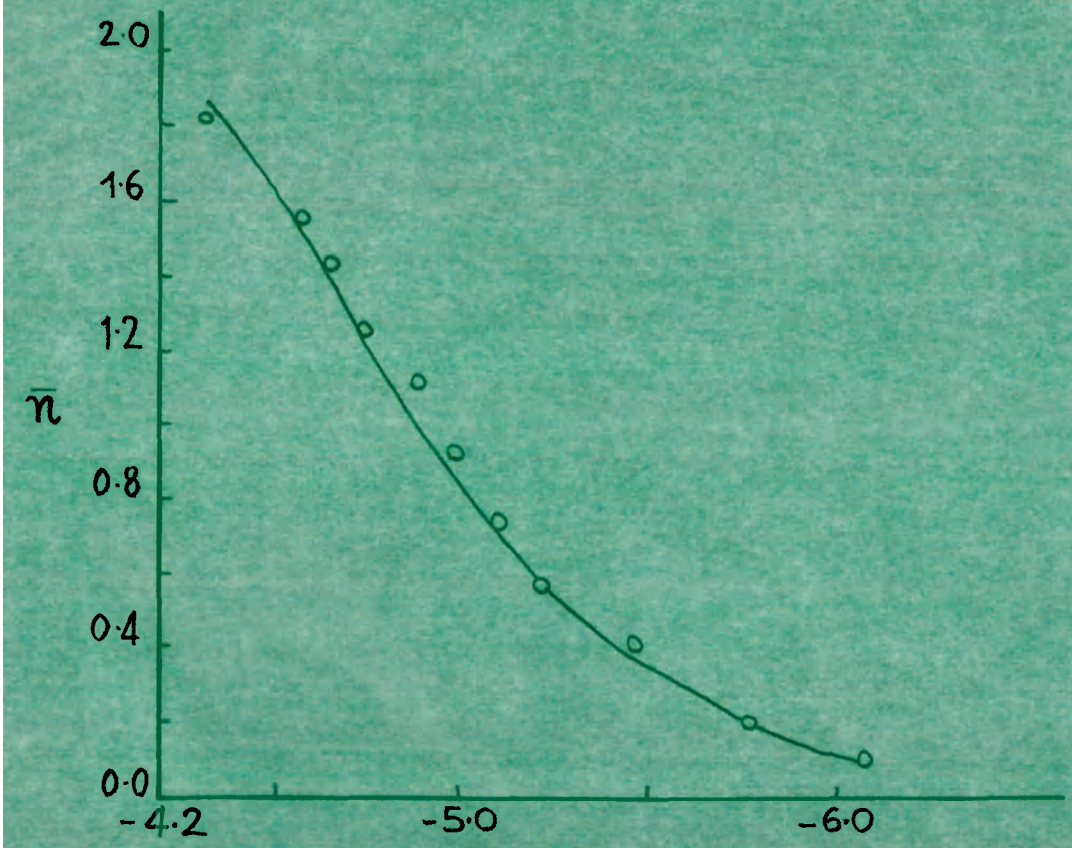
$\log K_s$ = 8.70 Graphically.

(Vide Fig. No.9 C)

FIGURE NO. 10C

FORMATION CURVE

CYSTEINE - $CrCl_2$ COMPLEX



VIDE TABLE NO. 10C

T A B L E No.10 C

pH-metric titration of Cysteine (0.01M ; pK_a = 10.28) and Chromium(II) Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.20	0.10	-6.0822	5.1252	xx
0.50	6.55	0.20	-5.7758	5.1783	xx
1.00	6.90	0.40	-5.4745	5.1500	xx
1.50	7.20	0.57	-5.2295	5.2923	xx
2.00	7.40	0.74	-5.0908	xx	xx
2.50	7.60	0.93	-4.9608	xx	xx
3.00	7.75	1.11	-4.8915	xx	xx
3.50	8.00	1.26	-4.7412	xx	4.5476
4.00	8.20	1.42	-4.6665	xx	4.6345
4.50	8.55	1.56	-4.4885	xx	4.6599
5.00	9.00	1.81	-4.3205	xx	xx

Mean log K' = 5.16

Mean log K" = 4.61

$\log K_s$ = 5.16 +4.61 = 9.77 Calculated

$\log K_s$ = 9.80 Graphically.

(Vide Fig. No. 10 C)

T A B L E No.11 C

pH-metric titration of DL-Methionine (0.01M; pK_a = 9.34) and Chromium(II) Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.65	xx	xx	xx	xx
0.25	5.95	0.10	-5.3922	-4.4356	xx
0.50	6.40	0.20	-4.9858	4.3783	xx
1.00	6.80	0.40	-4.6345	4.4420	xx
1.50	7.30	0.57	-4.1895	4.3343	xx
2.00	7.65	0.74	-3.9008	xx	xx
2.50	7.95	0.93	-3.6708	xx	xx
3.00	8.25	1.11	-3.4515	xx	xx
3.50	8.65	1.26	-3.1512	xx	2.9577
4.00	8.95	1.42	-2.9765	xx	2.9445
4.50	9.30	1.56	-2.7985	xx	2.9054
5.00	9.70	1.81	-2.6409	xx	xx

Mean log K' = 4.39

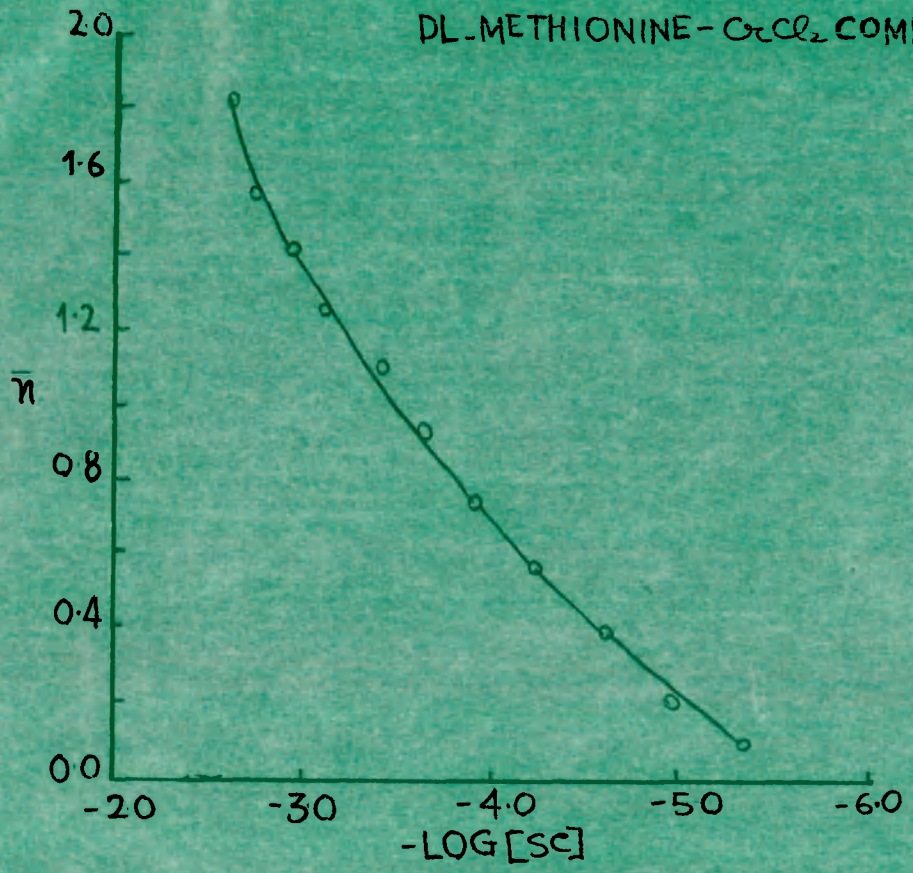
Mean log K" = 2.93

$\log K_s$ = 4.39 + 2.93 = 7.32 Calculated.

$\log K_s$ = 7.30 Graphically.

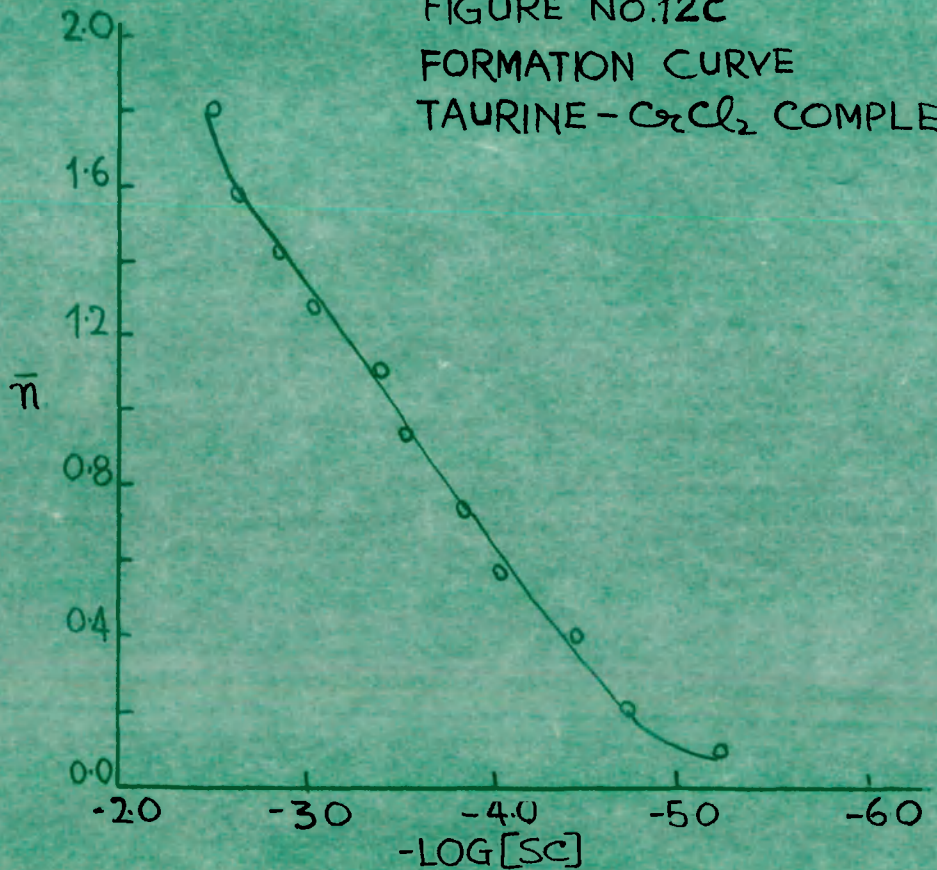
(Vide Fig. No. 11 C)

FIGURE NO. 11C
FORMATION CURVE
DL-METHIONINE - $CrCl_2$ COMPLEX



VIDE TABLE NO. 11C

FIGURE NO. 12C
FORMATION CURVE
TAURINE - $CrCl_2$ COMPLEX



VIDE TABLE NO. 12C

T A B L E No.12 C

pH-metric titration of Taurine (0.01M ; pK_a = 9.08) and Chromium(II) Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.55	xx	xx	xx	xx
0.25	5.80	0.10	-5.2822	4.1256	xx
0.50	6.30	0.20	-4.7758	4.1683	xx
1.00	6.70	0.40	-4.4745	4.2842	xx
1.50	7.15	0.57	-4.0795	4.2603	xx
2.00	7.45	0.74	-3.8408	xx	xx
2.50	7.80	0.93	-3.5608	xx	xx
3.00	8.10	1.11	-3.3415	xx	xx
3.50	8.50	1.26	-3.0412	xx	2.8476
4.00	8.85	1.42	-2.8165	xx	2.8845
4.50	9.20	1.56	-2.6385	xx	2.9096
5.00	9.55	1.81	-2.5709	xx	xx

Mean log K' = 4.20

Mean log K" = 2.86

$\log K_s$ = 4.20 + 2.86 = 7.06 Calculated

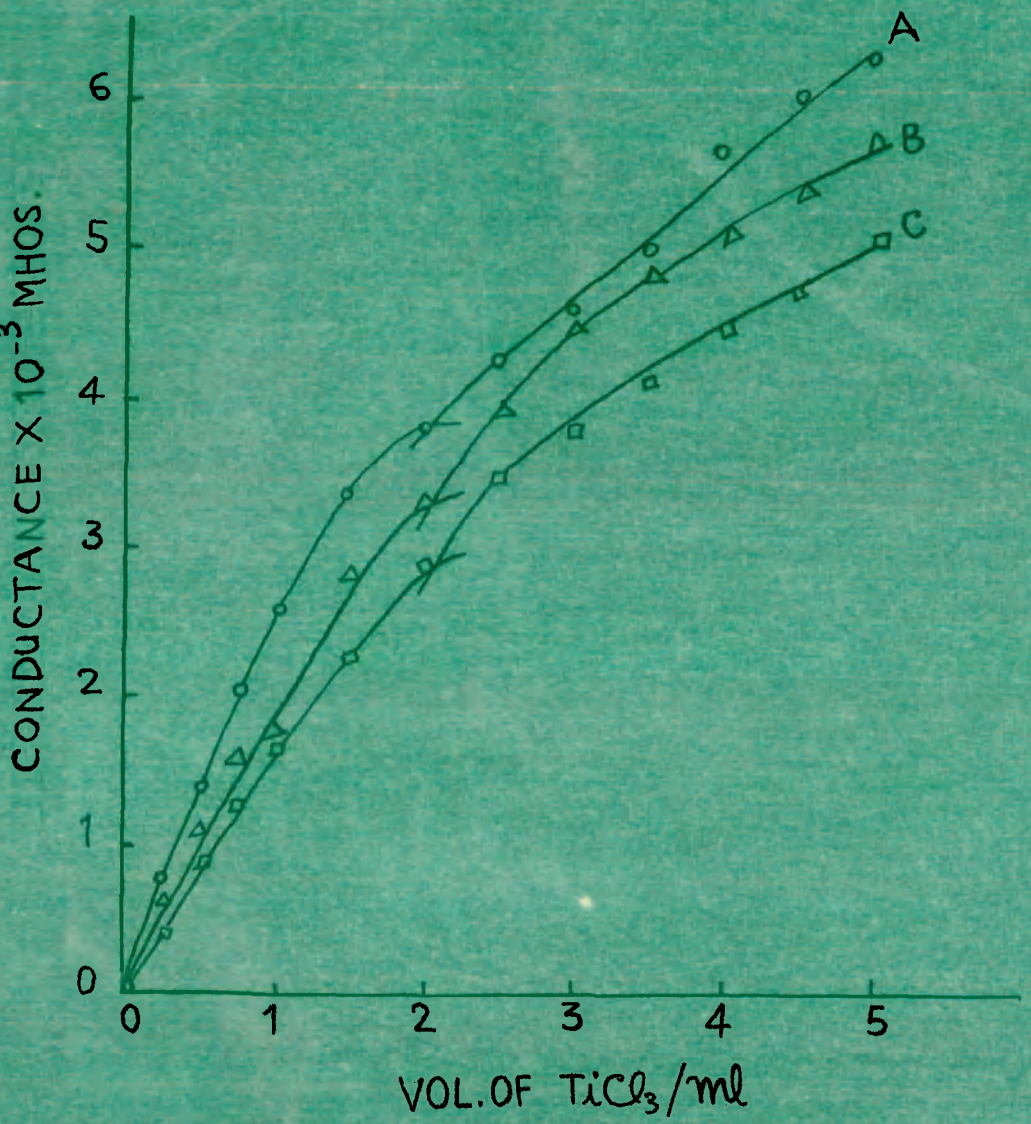
$\log K_s$ = 7.02 Graphically.

(Vide Fig. No.12 C)

FIGURE NO.13A

REVERSE CONDUCTOMETRIC TITRATIONS

GLYCINE - $TiCl_3$



A = 40 ml OF 0·005M GLYCINE Vs. 0·1M $TiCl_3$

B = 40 ml OF 0·0033 M GLYCINE Vs. 0·066M $TiCl_3$

C = 40 ml OF 0·0025M GLYCINE Vs. 0·05M $TiCl_3$

VIDE TABLE NO. 13A

T A B L E No.13 A

Conductometric - titrations (Reverse)

Glycine-Titanous Chloride Complex

Vol.of $TiCl_3$ added.(ml)	1st.titration.Conductance $x10^{-3}$mhos.	2nd.titration.Conductance $x10^{-3}$mhos.	3rd.titration.Conductance $x10^{-3}$mhos.
0.0	0.048	0.037	0.035
0.5	1.42	1.17	0.91
1.0	2.60	1.75	1.74
1.5	3.44	2.86	2.33
2.0	3.84	3.38	2.90
2.5	4.25	3.96	3.52
3.0	4.65	4.54	3.77
3.5	5.00	4.86	4.16
4.0	5.71	5.13	4.50
4.5	6.05	5.42	4.76
5.0	6.25	5.71	5.13

1st.titration :- 40 ml of 0.005M Glycine
Vs. 0.1M Titanous Chloride

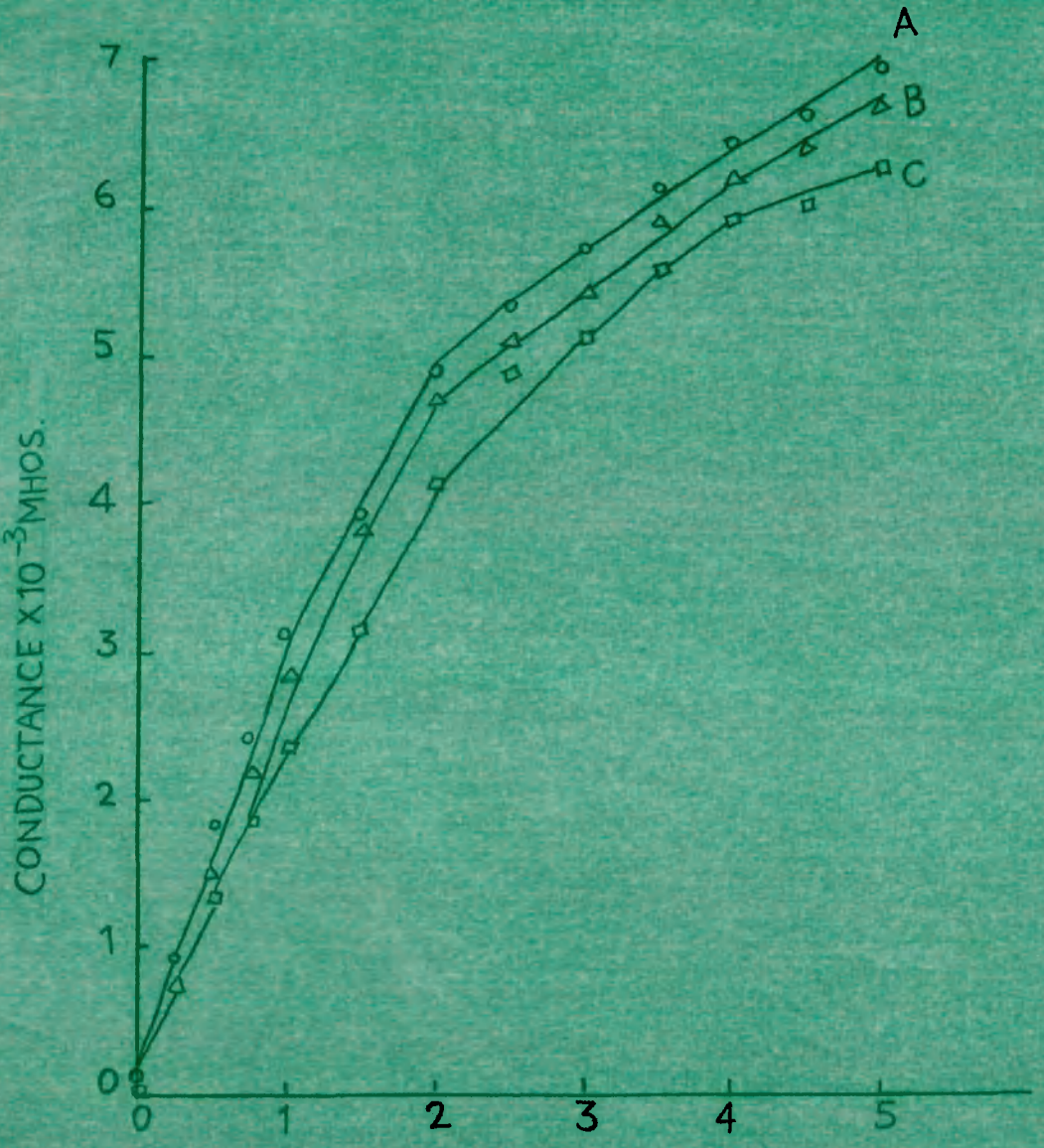
2nd.titration :- 40 ml of 0.0033M Glycine
Vs. 0.066M Titanous Chloride

3rd.titration :- 40 ml of 0.0025M Glycine
Vs. 0.05M Titanous Chloride

(Vide Fig. No.13 A)

FIGURE NO. 14 A

REVERSE CONDUCTOMETRIC TITRATIONS.



A = 40 ml OF 0·005 M DL-SERINE Vs. 0·1 M $TiCl_3$

B = 40 ml OF 0·0033 M DL-SERINE Vs. 0·066 M $TiCl_3$

C = 40 ml OF 0·0025 M DL-SERINE Vs. 0·05 M $TiCl_3$

VIDE TABLE NO. 14 A

T A B L E No.14 A

Conductometric - titrations (Reverse)
DL-Serine-Titanous Chloride Complex

Vol.of $TiCl_3$ Added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.06	0.04	0.02
0.5	1.82	1.50	0.98
1.0	3.15	2.85	2.35
1.5	3.95	3.85	3.15
2.0	4.90	4.70	4.22
2.5	5.35	5.10	4.80
3.0	5.75	5.45	5.15
3.5	6.16	5.95	5.60
4.0	6.48	6.20	5.95
4.5	6.65	6.40	6.00
5.0	6.95	6.72	6.25

1st.titration :- 40 ml of 0.005M DL- Serine
Vs. 0.1M Titanous Chloride

2nd.titration :- 40 ml of 0.0033M DL- Serine
Vs. 0.066M Titanous Chloride

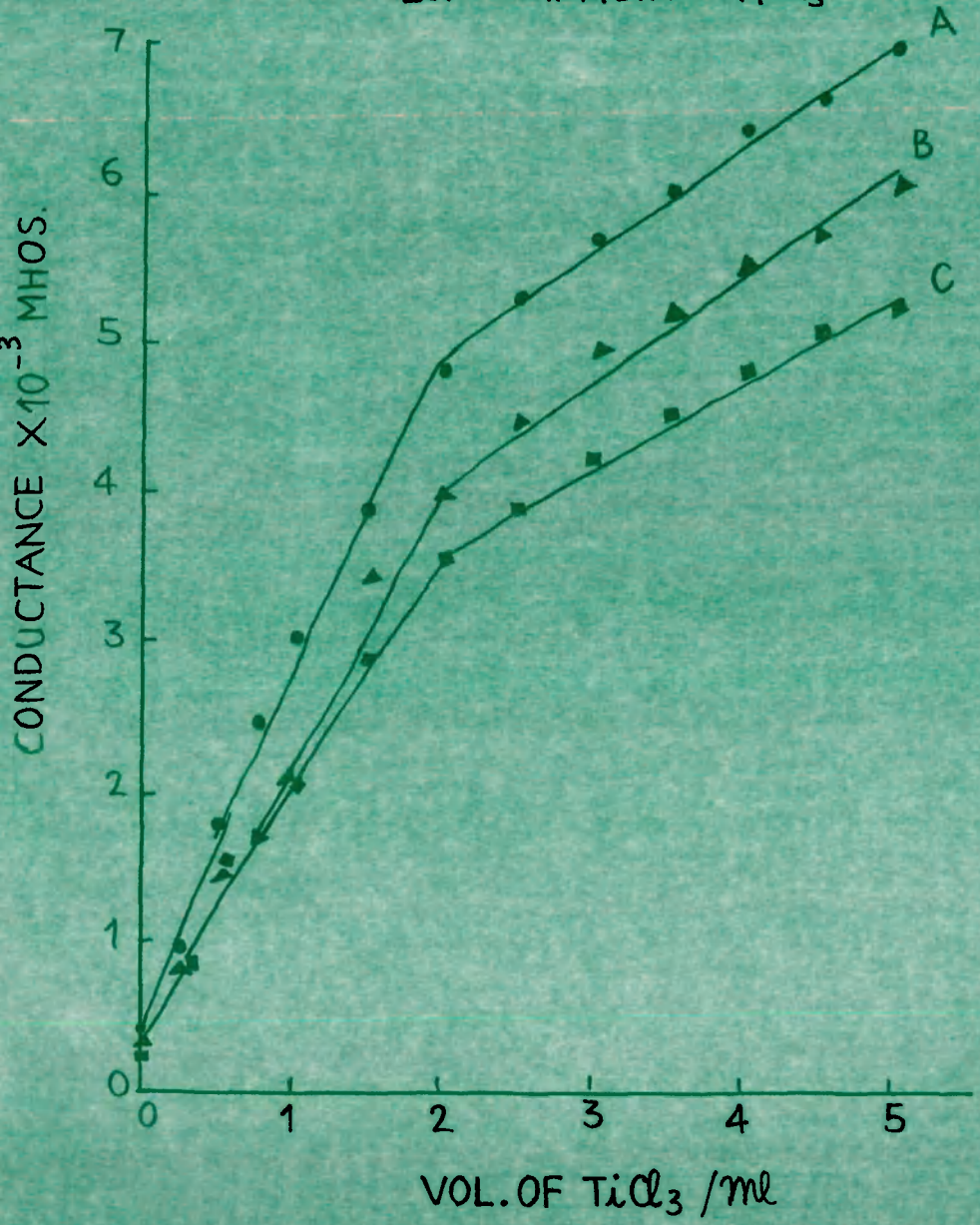
3rd.titration :- 40 ml of 0.0025M DL- Serine
Vs. 0.05M Titanous Chloride

(Vide Fig. No.14 A)

FIGURE NO.15A

REVERSE CONDUCTOMETRIC TITRATIONS.

L-ASPARAGINE - $TiCl_3$



A = 40 OF 0·005 M L-ASPARAGINE VS. 0·1 M $TiCl_3$

B = 40 ml OF 0·0033 ML-ASPARAGINE Vs. 0·066 M $TiCl_3$

C = 40 ml OF 0·0025 ML-ASPARAGINE Vs. 0·05 M $TiCl_3$

VIDE TABLE NO.15A

T A B L E No.15 A

Conductometric - titrations (Reverse)
L-Asparagine-Titanous Chloride Complex

Vol.of $TiCl_3$ added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.04	0.037	0.03
0.5	1.80	1.46	1.50
1.0	3.12	2.13	2.17
1.5	3.92	3.45	2.90
2.0	4.86	4.00	3.56
2.5	5.30	4.50	3.92
3.0	5.70	5.00	4.25
3.5	6.06	5.25	4.55
4.0	6.45	5.55	4.86
4.5	6.66	5.71	5.13
5.0	6.75	6.06	5.25

1st.titration :- 40 ml of 0.005M L-Asparagine
Vs. 0.1M Titanous Chloride

2nd.titration :- 40 ml of 0.0033M L-Asparagine
Vs. 0.066M Titanous Chloride

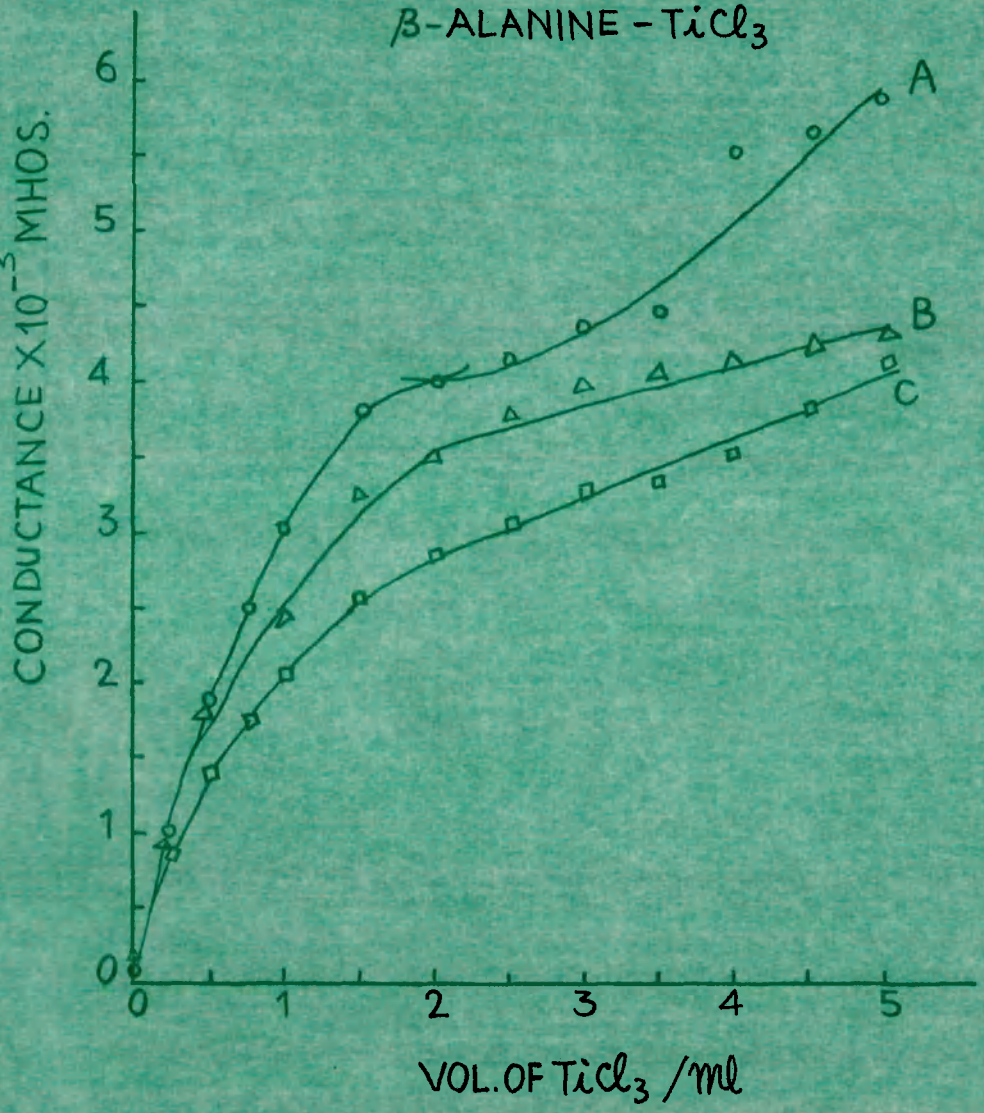
3rd.titration :- 40 ml of 0.0025M L-Asparagine
Vs. 0.05M Titanous Chloride

(Vide Fig. No.15 A)

FIGURE NO. 16A

REVERSE CONDUCTOMETRIC TITRATIONS.

β-ALANINE - $TiCl_3$



A = 40 ml OF 0·005 M β-ALANINE Vs.
0·1 M $TiCl_3$

B = 40 ml OF 0·0033 M β-ALANINE Vs.
0·066 M $TiCl_3$

C = 40 ml OF 0·0025 M β-ALANINE Vs.
0·05 M $TiCl_3$

VIDE TABLE NO. 16A

T A B L E No.16 A

Conductometric - titrations (Reverse)
β-Alanine Titanous Chloride Complex

Vol.of $TiCl_3$ added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.037	0.033	0.026
0.5	1.85	1.82	1.43
1.0	3.03	2.44	2.08
1.5	3.84	3.23	2.56
2.0	4.00	3.50	2.85
2.5	4.16	3.77	3.03
3.0	4.35	4.00	3.23
3.5	4.45	4.08	3.33
4.0	5.55	4.15	3.50
4.5	5.65	4.25	3.84
5.0	5.87	4.35	4.15

1st.titration :- 40 ml of 0.005M β-Alanine Vs. 0.1M Titanous Chloride

2nd.titration :- 40 ml of 0.0033M β-Alanine Vs. 0.0066M Titanous Chloride

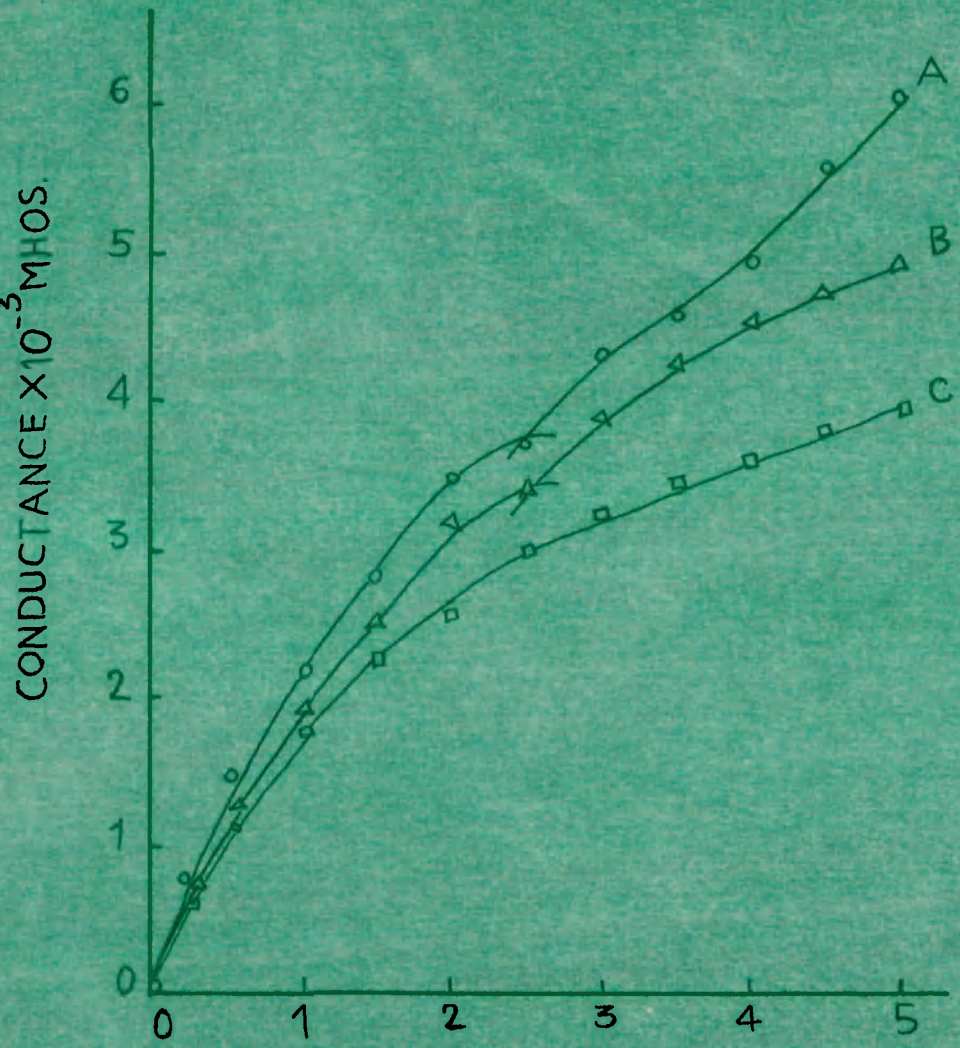
3rd.titration :- 40 ml of 0.0025M β-Alanine Vs. 0.05M Titanous Chloride

(Vide Fig. No.16 A)

FIGURE NO. 17A

REVERSE CONDUCTOMETRIC TITRATIONS

L-PROLINE - $TiCl_3$



A = 50 ml OF 0·005 M L-PROLINE Vs 0·1 M $TiCl_3$

B = 50 ml OF 0·0033 M L-PROLINE Vs. 0·066 M $TiCl_3$

C = 50 ml OF 0·0025 M L-PROLINE Vs. 0·05 M $TiCl_3$

VIDE TABLE No. 17A

TABLE No.17 A

Conductometric - titrations (Reverse)

L- Proline - Titanous Chloride Complex

Vol. of $TiCl_3$ added. (ml)	1st.titration. Conductance $x10^{-3}$ mhos	2nd.titration. Conductance $x10^{-3}$ mhos.	3rd.titration. Conductance $x10^{-3}$ mhos.
0.0	0.05	0.045	0.035
0.5	1.50	1.38	1.20
1.0	2.20	1.95	1.80
1.5	2.80	2.50	2.25
2.0	3.50	3.20	2.65
2.5	3.70	3.40	3.00
3.0	4.30	3.90	3.25
3.5	4.60	4.25	3.45
4.0	4.95	4.50	3.60
4.5	5.60	4.70	3.80
5.0	6.00	4.95	3.95

1st.titration :- 50 ml of 0.005M L-Proline
Vs. 0.1M Titanous Chloride

2nd.titration :- 50 ml of 0.0033M L-Proline
Vs. 0.066M Titanous Chloride

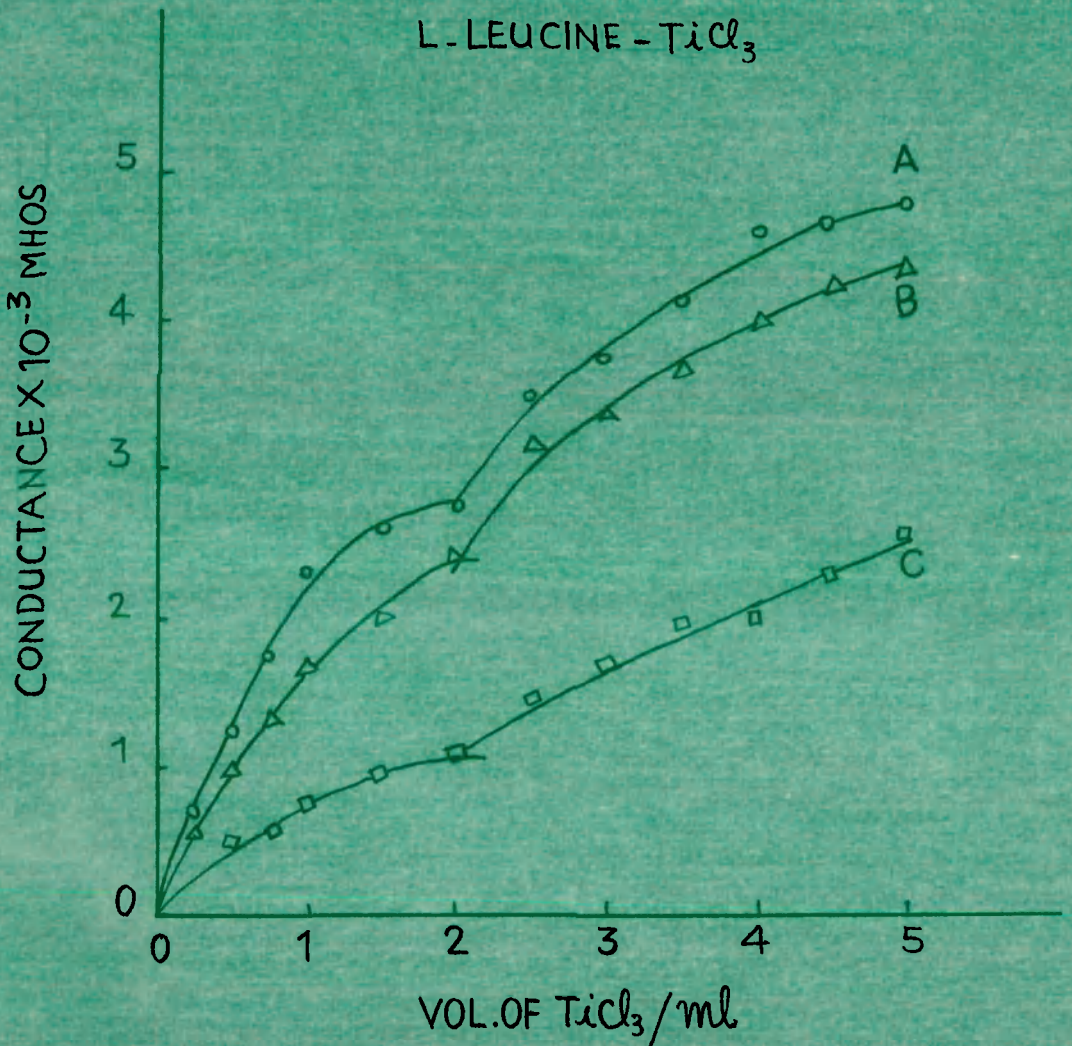
3rd.titration :- 50 ml of 0.0025M L-Proline
Vs. 0.05M Titanous Chloride

(Vide Fig. No.17 A)

FIGURE NO. 18 A

REVERSE CONDUCTOMETRIC TITRATIONS

L-LEUCINE - $TiCl_3$



A = 40 ml OF 0·005 M L-LEUCINE Vs. 0·1 M $TiCl_3$

B = 40 ml OF 0·0033 M L-LEUCINE Vs. 0·066 M $TiCl_3$

C = 40 ml OF 0·0025 M L-LEUCINE Vs. 0·05 M $TiCl_3$

VIDE TABLE NO. 18A

T A B L E No.18 A

Conductometric - titrations (Reverse)

L- Leucine - Titanous Chloride Complex.

Vol.of $TiCl_3$ added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.028	0.02	0.02
0.5	1.25	1.00	0.50
1.0	2.33	1.70	0.75
1.5	2.60	2.00	0.95
2.0	2.75	2.40	1.05
2.5	3.50	3.20	1.45
3.0	3.75	3.40	1.70
3.5	4.10	3.70	2.00
4.0	4.60	4.00	2.00
4.5	4.65	4.25	2.30
5.0	4.75	4.30	2.60

1st.titration :- 40 ml of 0.005M L-Leucine
Vs. 0.1M Titanous Chloride

2nd.titration :- 40 ml of 0.003M L-Leucine
Vs. 0.066M Titanous Chloride

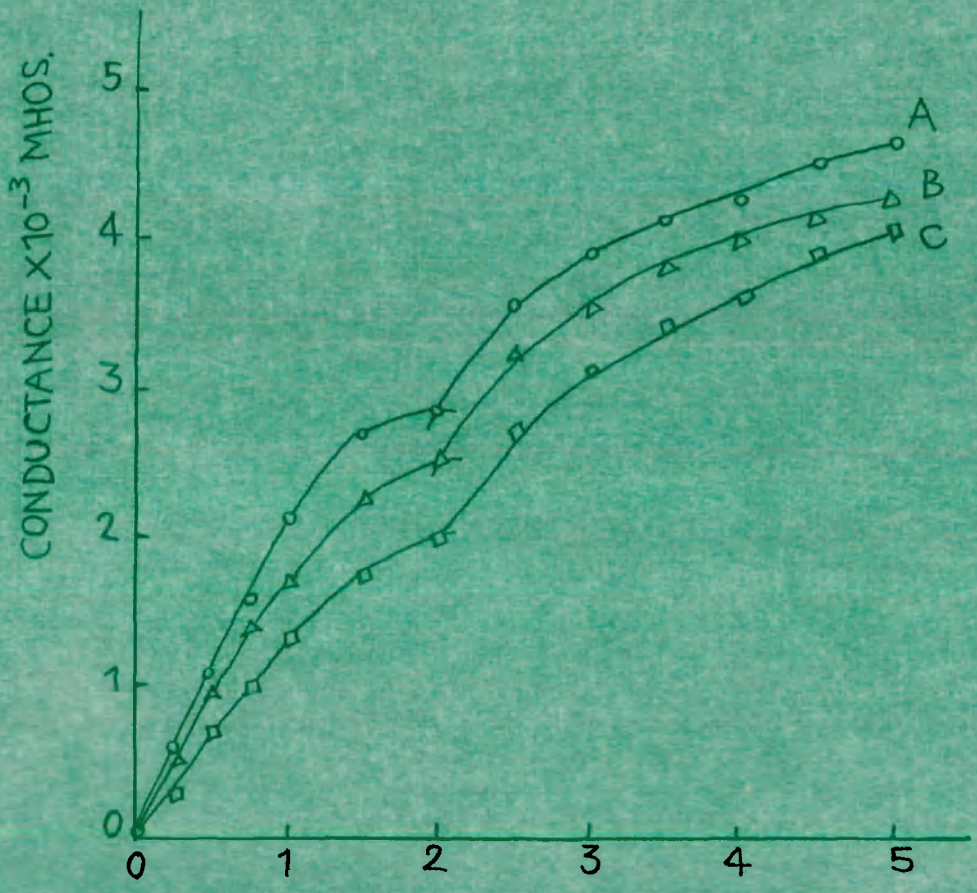
3rd.titration :- 40 ml of 0.0025M L-Leucine
Vs. 0.05M Titanous Chloride

(Vide Fig. No.18 A)

FIGURE NO. 19A

REVERSE CONDUCTOMETRIC TITRATIONS

DL-α-ALANINE-$TiCl_3$



A = 40 ml OF 0·005 M DL-α-ALANINE Vs. 0·1M $TiCl_3$

B = 40 ml OF 0·0033 M DL-α-ALANINE Vs. 0·066 M $TiCl_3$

C = 40 ml OF 0·0025 M DL-α-ALANINE Vs. 0·05 M $TiCl_3$

VIDE TABLE NO. 19A

T A B L E No.19 A

Conductometric - titrations (Reverse)

DL- ∝-Alanine-Titanous Chloride Complex

Vol.of $TiCl_3$ added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.09	0.085	0.071
0.5	1.11	1.00	0.71
1.0	2.17	1.72	1.33
1.5	2.70	2.27	1.75
2.0	3.86	2.54	2.00
2.5	3.57	3.22	2.70
3.0	3.92	3.57	3.13
3.5	4.16	3.77	3.44
4.0	4.24	4.00	3.64
4.5	4.54	4.16	3.92
5.0	4.65	4.26	4.07

1st.titration :- 40 ml of 0.005M DL- ∝-Alanine
Vs. 0.1M Titanous Chloride

2nd.titration :- 40 ml of 0.0033M DL-∝-Alanine
Vs. 0.066M Titanous Chloride

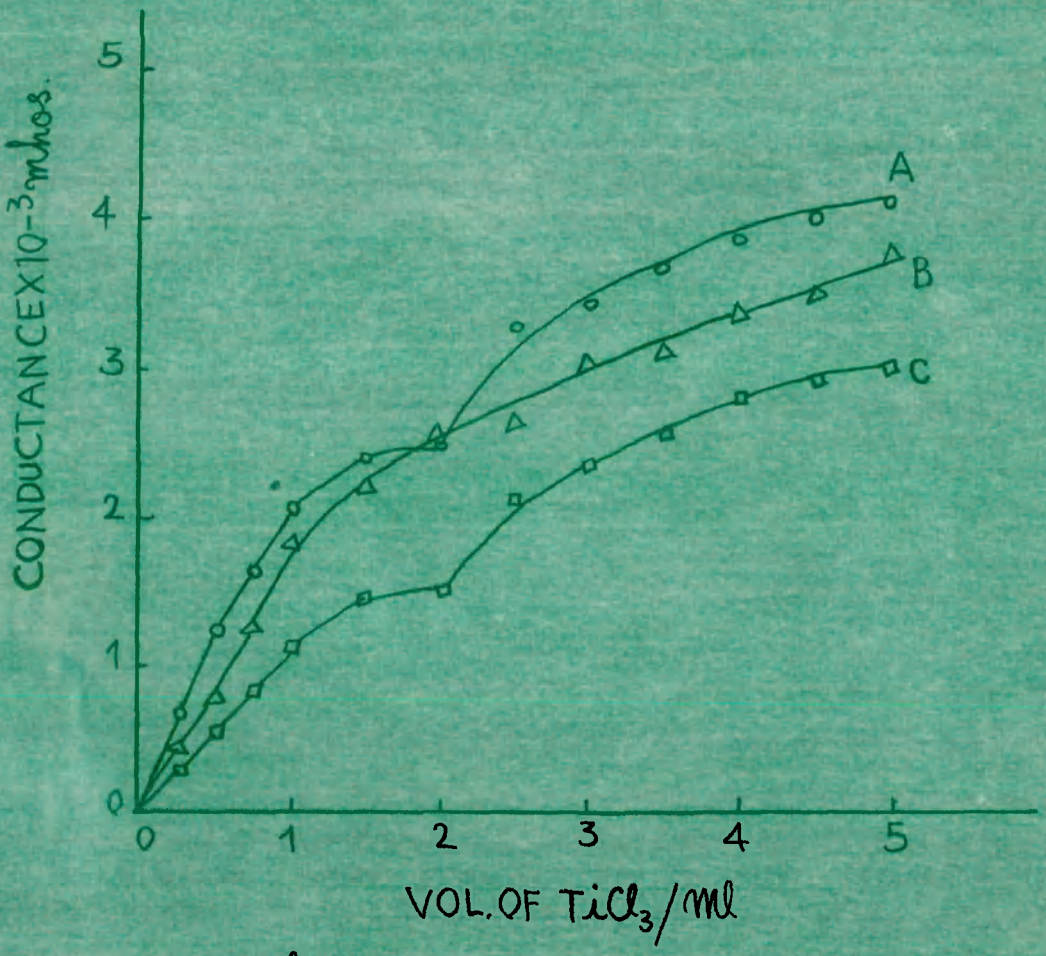
3rd.titration :- 40 ml of 0.0025M DL- ∝-Alanine
Vs. 0.05M Titanous chloride

(Vide Fig. No.19 A)

FIGURE NO. 20A

REVERSE CONDUCTOMETRIC TITRATIONS

DL-VALINE - $TiCl_3$



A = 40 ml OF 0·005 M DL-VALINE VS. 0·1 M $TiCl_3$

B = 40 ml OF 0·0033 M DL VALINE VS. 0·066 M $TiCl_3$

C = 40 ml OF 0·0025 M DL-VALINE VS. 0·05 M $TiCl_3$

VIDE TABLE NO. 20A

TABLE No. 20 A

Conductometric - titrations (Reverse)
DL-Valine - Titanous Chloride Complex

Vol.of $TiCl_3$ added.(ml)	1st.titration. Conductance $x10^{-3}$mhos.	2nd.titration. Conductance $x10^{-3}$mhos.	3rd.titration. Conductance $x10^{-3}$mhos.
0.0	0.038	0.035	0.03
0.5	1.25	0.77	0.58
1.0	2.06	1.84	1.18
1.5	2.47	2.22	1.46
2.0	2.50	2.56	1.50
2.5	3.23	2.58	2.18
3.0	3.44	3.03	2.38
3.5	3.71	3.17	2.56
4.0	3.84	3.44	2.81
4.5	4.00	3.50	2.90
5.0	4.16	3.75	2.98

1st.titration :- 40 ml of 0.005M DL- Valine
Vs. 0.1M Titanous Chloride

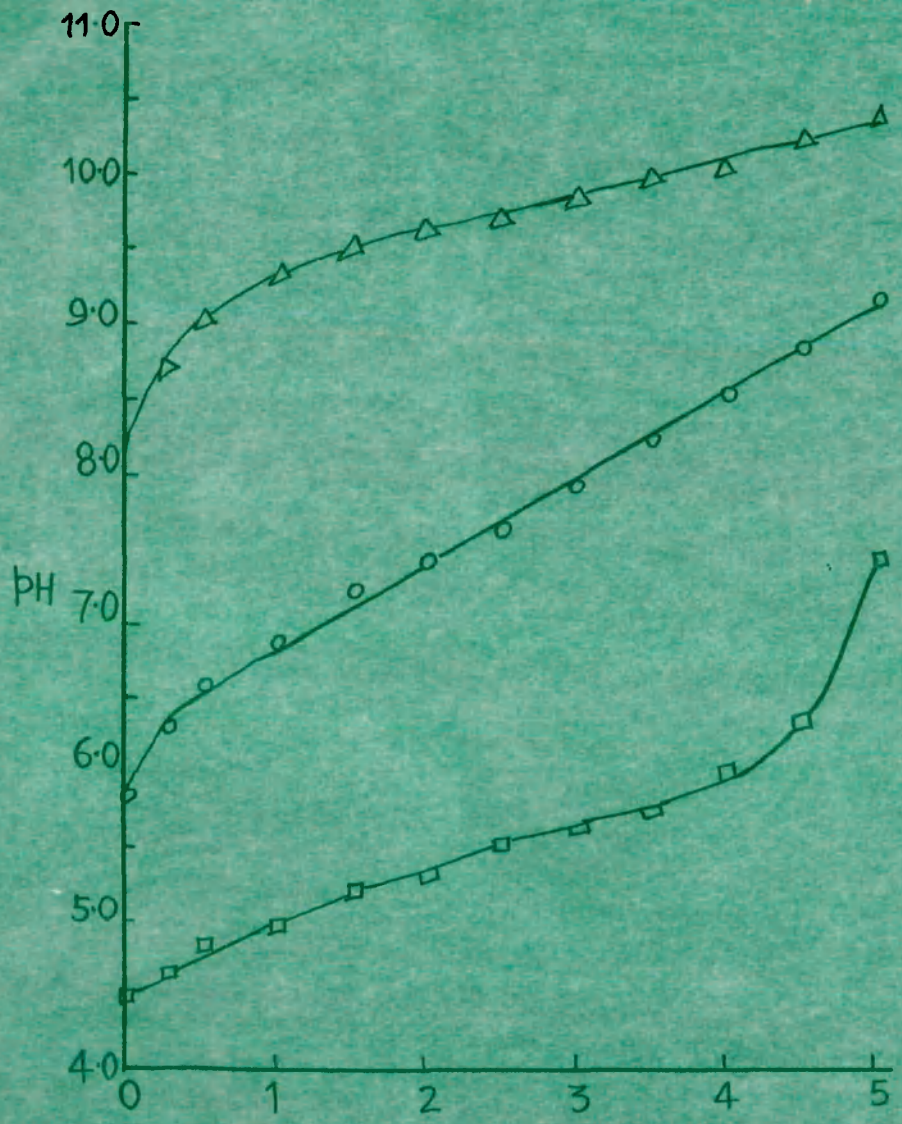
2nd.titration :- 40 ml of 0.0033M DL-Valine
Vs. 0.066M Titanous Chloride

3rd.titration :- 40 ml of 0.0025M DL-Valine
Vs. 0.05M Titanous Chloride

(Vide Fig. No.20 A)

FIGURE NO. 13B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M GLYCINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02M GLYCINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO. 13B

TABLE No.13 B

pH-metric titrations of Ti(III) Glycine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	4.50	5.85
0.25	8.70	4.65	6.30
0.50	9.00	4.85	6.60
1.00	9.30	4.95	6.85
1.50	9.50	5.20	7.20
2.00	9.60	5.30	7.40
2.50	9.70	5.50	7.65
3.00	9.80	5.60	7.90
3.50	9.90	5.70	8.20
4.00	10.00	6.00	8.50
4.50	10.20	6.30	8.80
5.00	10.35	7.40	9.15

(A) = 50 ml of 0.01M Glycine (in the cell)

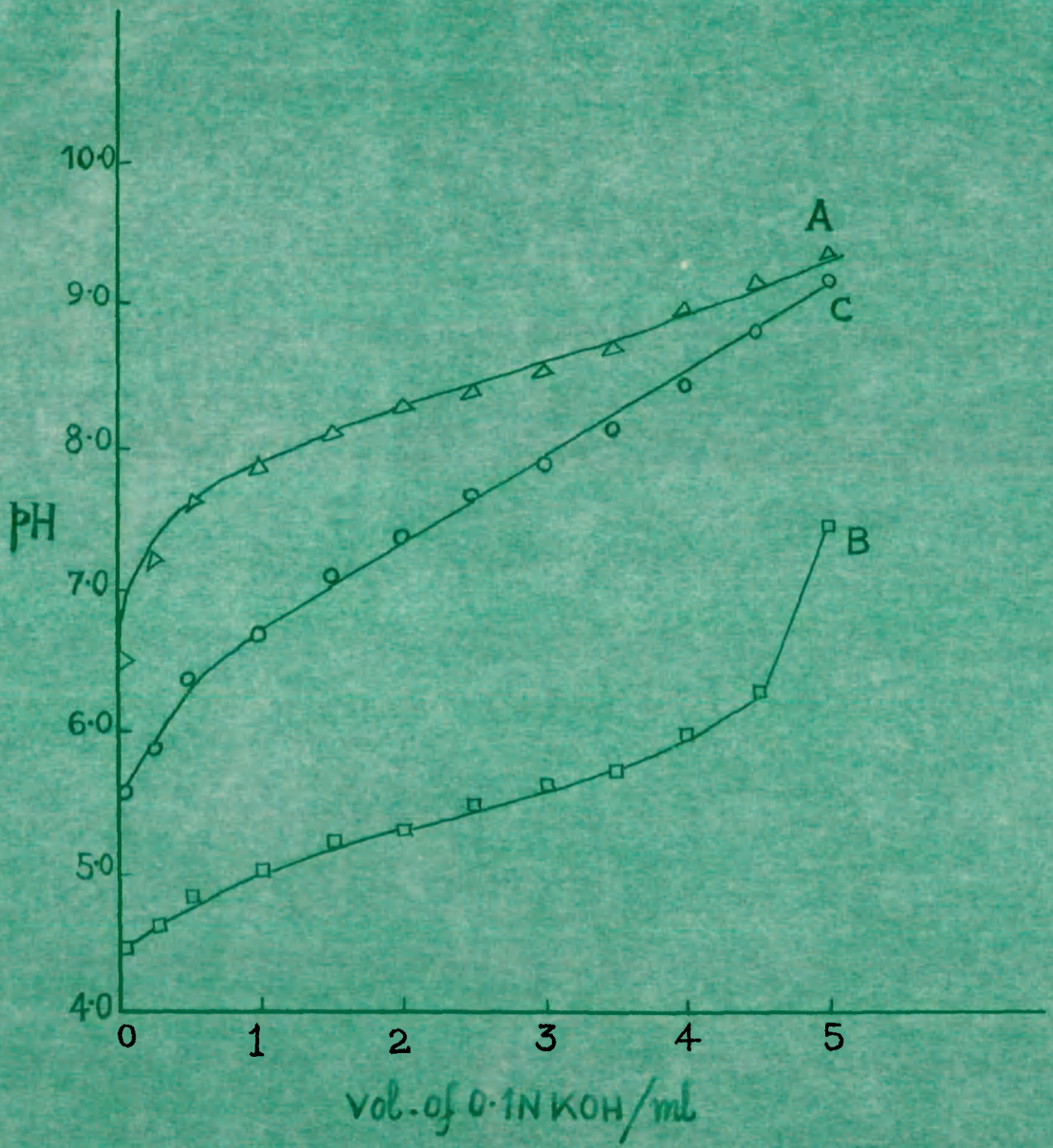
(B) = 50 ml of 0.005M Titanous Chloride (in the cell)

(C) = 25 ml of 0.02M Glycine + 25 ml of 0.005M Titanous Chloride (in the cell)

(Vide Fig. No.13 B)

FIGURE No.14B

pH-METRIC TITIRATIONS



A = 50 ml of 0·01M DL-Serine. (in the cell)

B = 50 ml of 0·005M $TiCl_3$. (in the cell)

C = 25 ml of 0·02 MDL-Serine + 25ml of 0·01M $TiCl_3$ (in the cell)

Vide table. NO 14B

T A B L E No.14 B

pH-metric titrations of Ti(III)-DL-Serine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	4.50	5.60
0.25	7.40	4.65	5.90
0.50	7.60	4.85	6.40
1.00	7.90	5.00	6.70
1.50	8.20	5.20	7.10
2.00	8.30	5.30	7.35
2.50	8.40	5.50	7.65
3.00	8.50	5.60	7.85
3.50	8.70	5.70	8.10
4.00	8.95	5.95	8.40
4.50	9.20	6.25	8.80
5.00	9.30	7.40	9.15

(A) = 50 ml of 0.01M DL- Serine (in the cell)

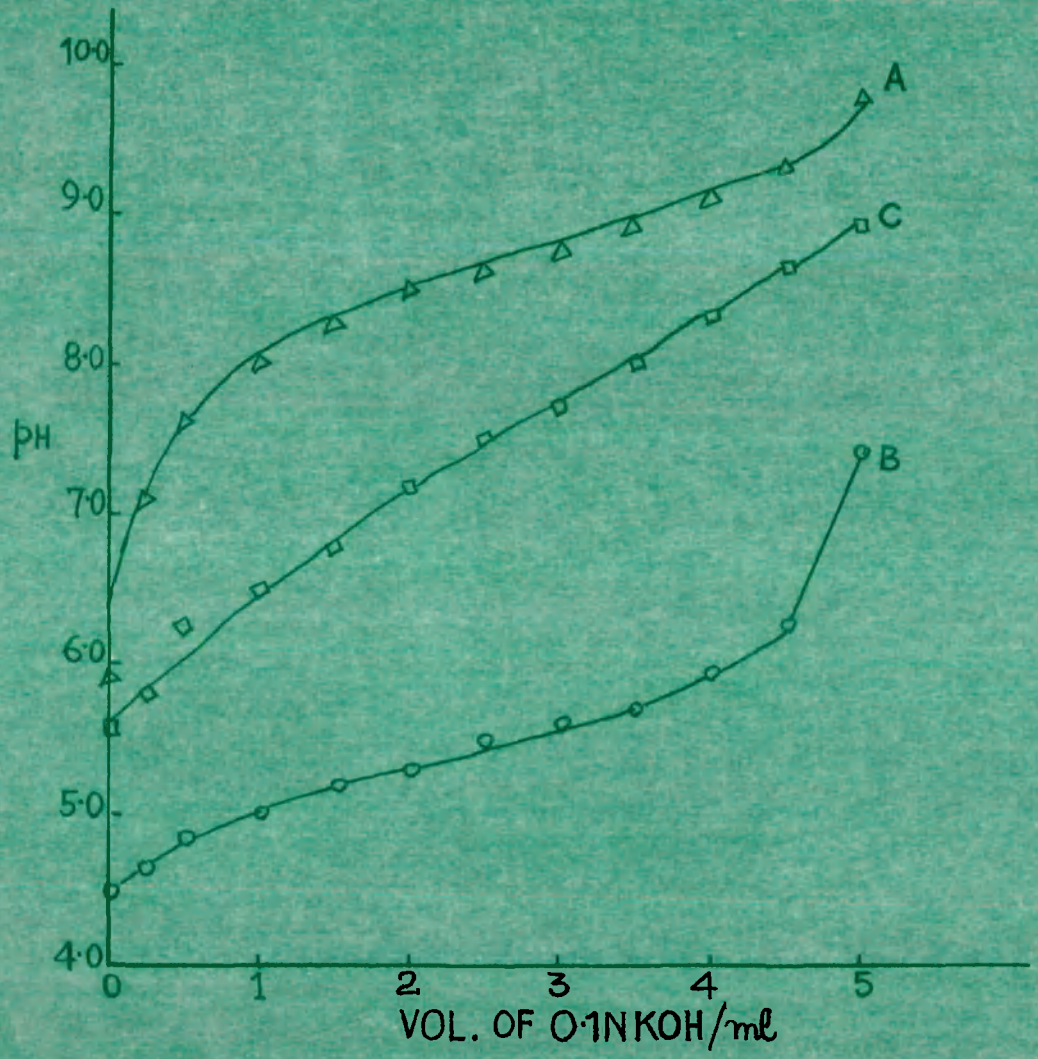
(B) = 50 ml of 0.005M Titanous Chloride(in the cell)

(C) = 25 ml of 0.02M DL-Serine + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.14 B)

FIGURE No.15 B

PH-METRIC TITRATIONS



A = 50 ml OF 0·01 M L-ASPARAGINE (IN THE CELL)

B = 50 ml OF 0·005 M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02 M L-ASPARAGINE + 25 ml OF 0.01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO.15 B

T A B L E No.15 B

pH-metric titrations of Ti(III)-L-Asparagine System

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	4.50	5.55
0.25	7.10	4.65	5.80
0.50	7.60	4.85	6.25
1.00	8.00	5.00	6.50
1.50	8.25	5.20	6.80
2.00	8.50	5.30	7.20
2.50	8.60	5.50	7.50
3.00	8.70	2.60	7.70
3.50	8.90	5.70	8.00
4.00	9.10	5.95	8.30
4.50	9.30	6.25	8.65
5.00	9.75	7.40	9.00

(A) = 50 ml of 0.01M L-Asparagine (in the cell)

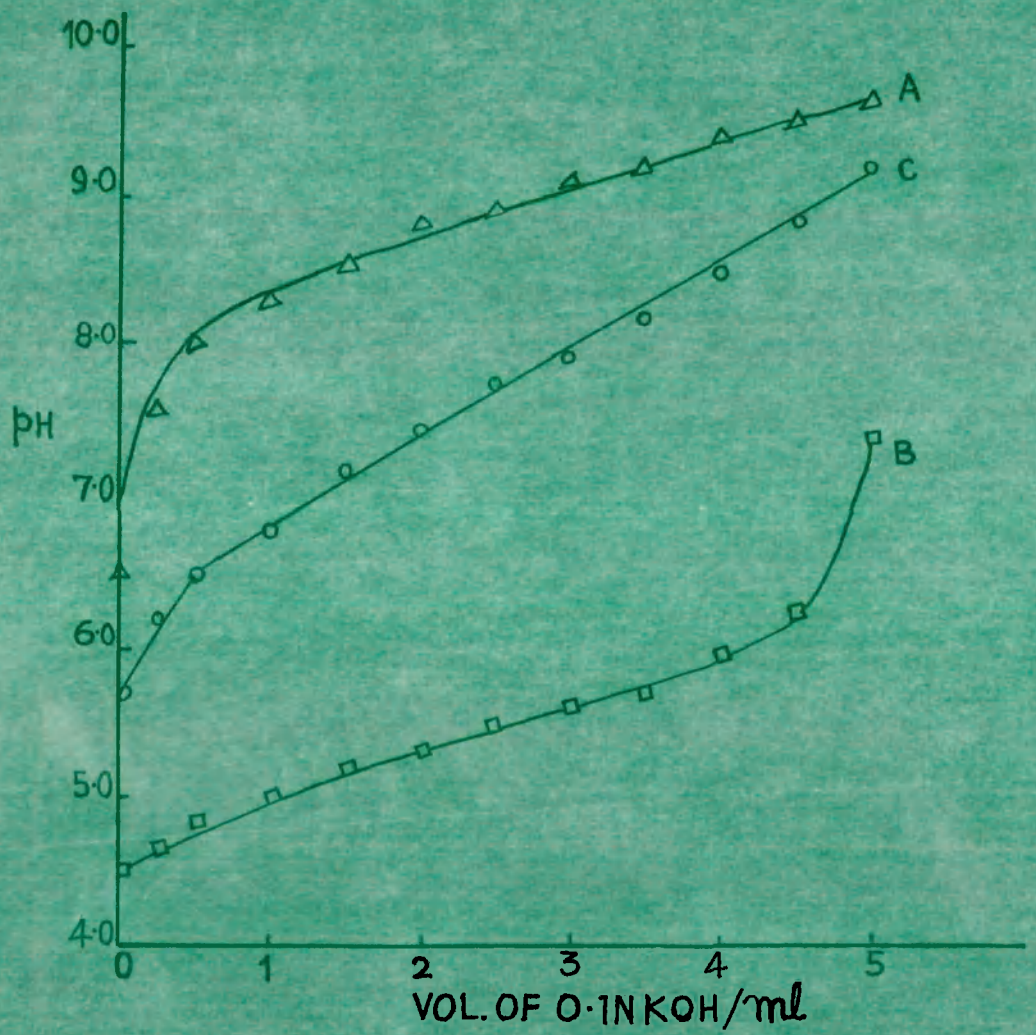
(B) = 50 ml of 0.005M Titanous Chloride(in the cell)

(C) = 25 ml of 0.02M L-Asparagine + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.15 B)

FIGURE NO. 16 B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M β-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02M β-ALANINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO. 16 B

T A B L E No.16 B

pH-metric titrations of Ti(III)-β-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	4.50	5.70
0.25	7.60	4.75	6.20
0.50	8.05	4.85	6.50
1.00	8.30	5.00	6.80
1.50	8.55	5.20	7.20
2.00	8.80	5.30	7.45
2.50	8.90	5.50	7.75
3.00	9.10	5.60	7.95
3.50	9.20	5.70	8.20
4.00	9.40	5.95	8.50
4.50	9.50	6.25	8.85
5.00	9.60	7.40	9.20

(A) = 50 ml of 0.01M β-Alanine (in the cell)

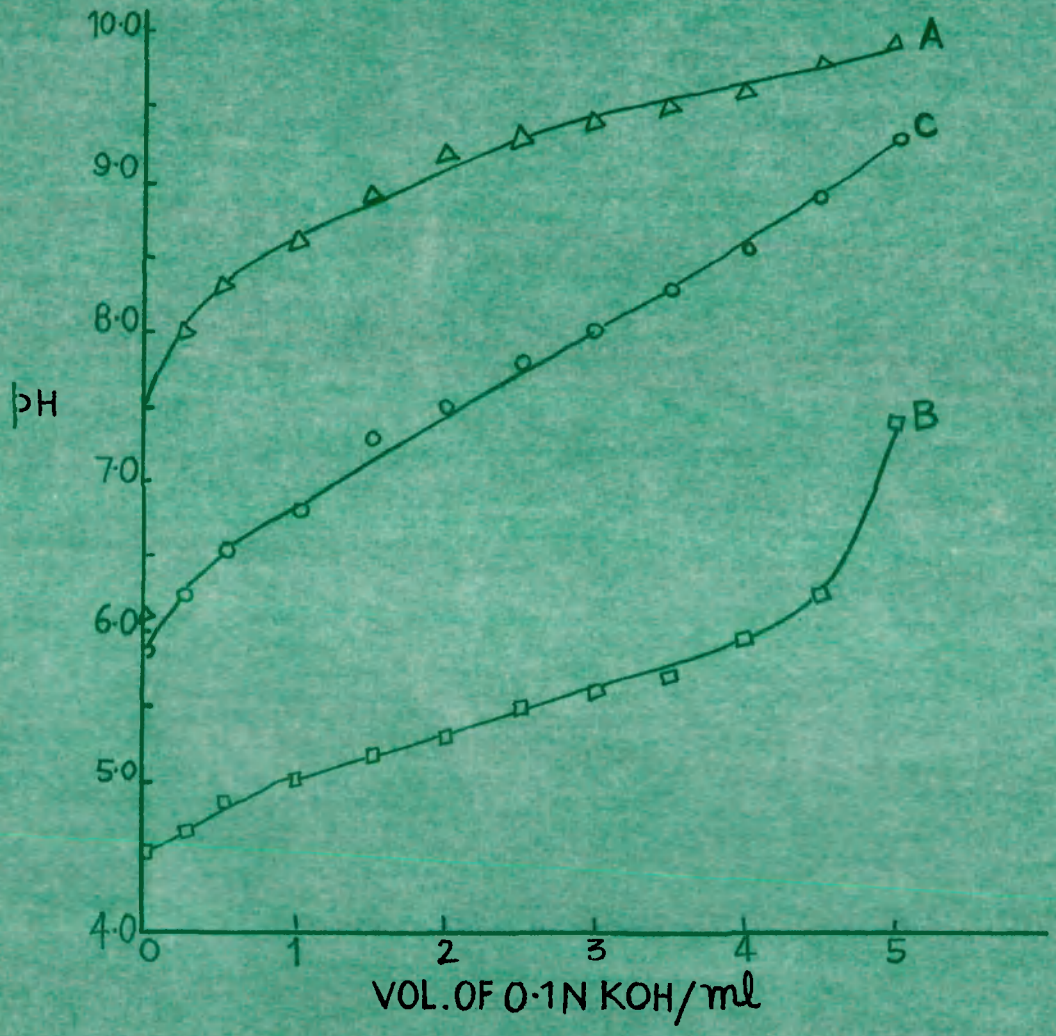
(B) = 50 ml of 0.005M Titanous Chloride(in the cell)

(C) = 25 ml of 0.02M β-Alanine + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.16 B)

FIGURE NO. 17B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-PROLINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02M L-PROLINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE No. 17B

T A B L E No.17 B

pH-metric titrations of Ti(III)-L-Proline system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.10	4.50	5.85
0.25	8.00	4.65	6.25
0.50	8.30	4.85	6.55
1.00	8.60	5.00	6.80
1.50	8.90	5.20	7.30
2.00	9.20	5.30	7.50
2.50	9.30	5.50	7.80
3.00	9.40	5.60	8.00
3.50	9.50	5.70	8.30
4.00	9.60	5.95	8.55
4.50	9.80	6.25	8.90
5.00	9.90	7.40	9.30

(A) = 50 ml of 0.01M L-Proline (in the cell)

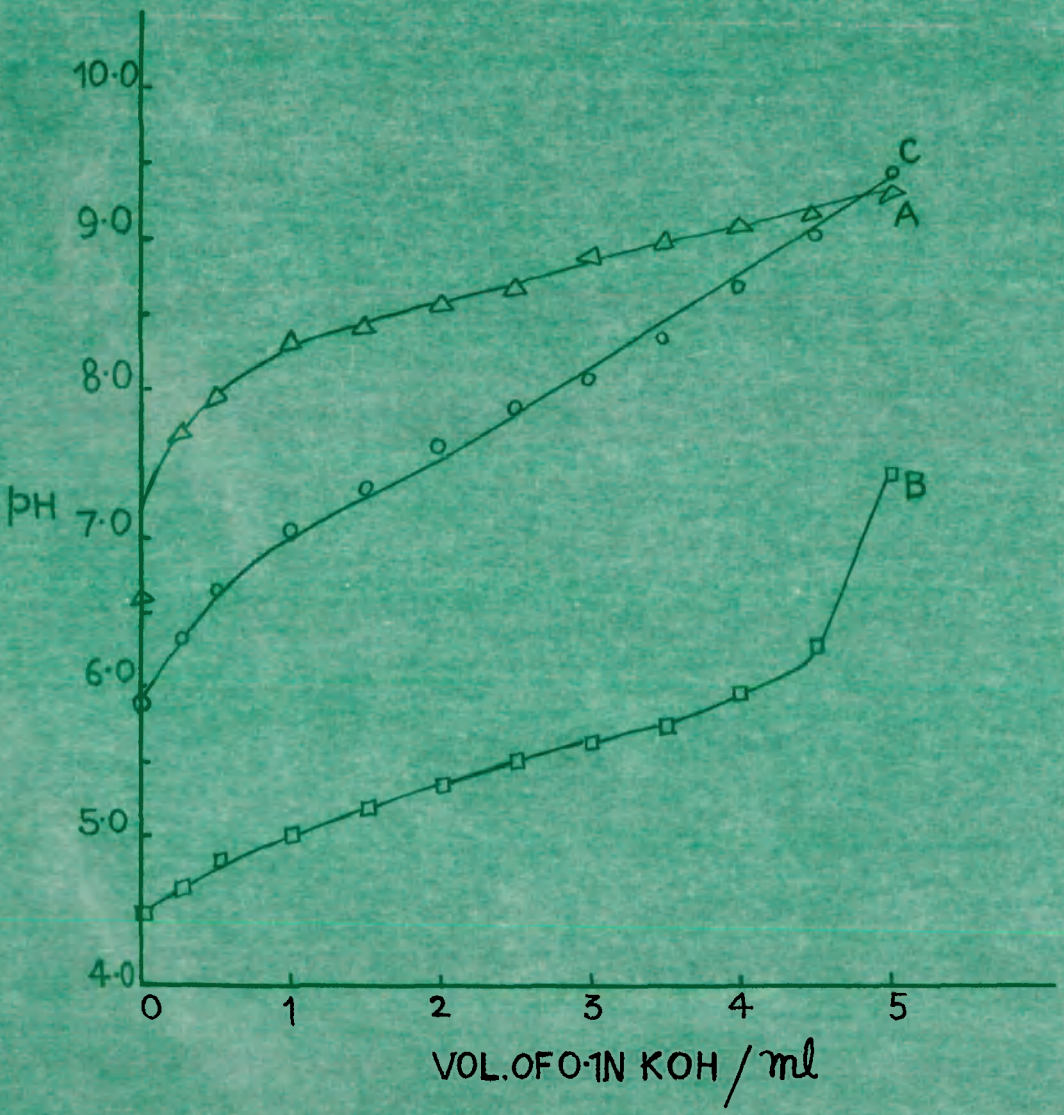
(B) = 50 ml of 0.005M Titanous Chloride(in the cell)

(C) = 25 ml of 0.02M L-Proline + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.17 B)

FIGURE NO. 18 B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01ML-LEUCINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_2$ (IN THE CELL)

C = 25 ml OF 0·02ML-LEUCINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO. 18B

T A B L E No.18 B

pH-metric titrations of Ti(III)-L-Leucine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.60	4.50	5.90
0.25	7.70	4.65	6.34
0.50	7.90	4.85	6.68
1.00	8.30	5.00	7.05
1.50	8.40	5.20	7.32
2.00	8.55	5.30	7.63
2.50	8.65	5.50	7.85
3.00	8.85	5.60	8.02
3.50	8.95	5.70	8.32
4.00	9.05	5.95	8.65
4.50	9.15	6.25	9.05
5.00	9.30	7.40	9.40

(A) = 50 ml of 0.01M L-Leucine (in the cell)

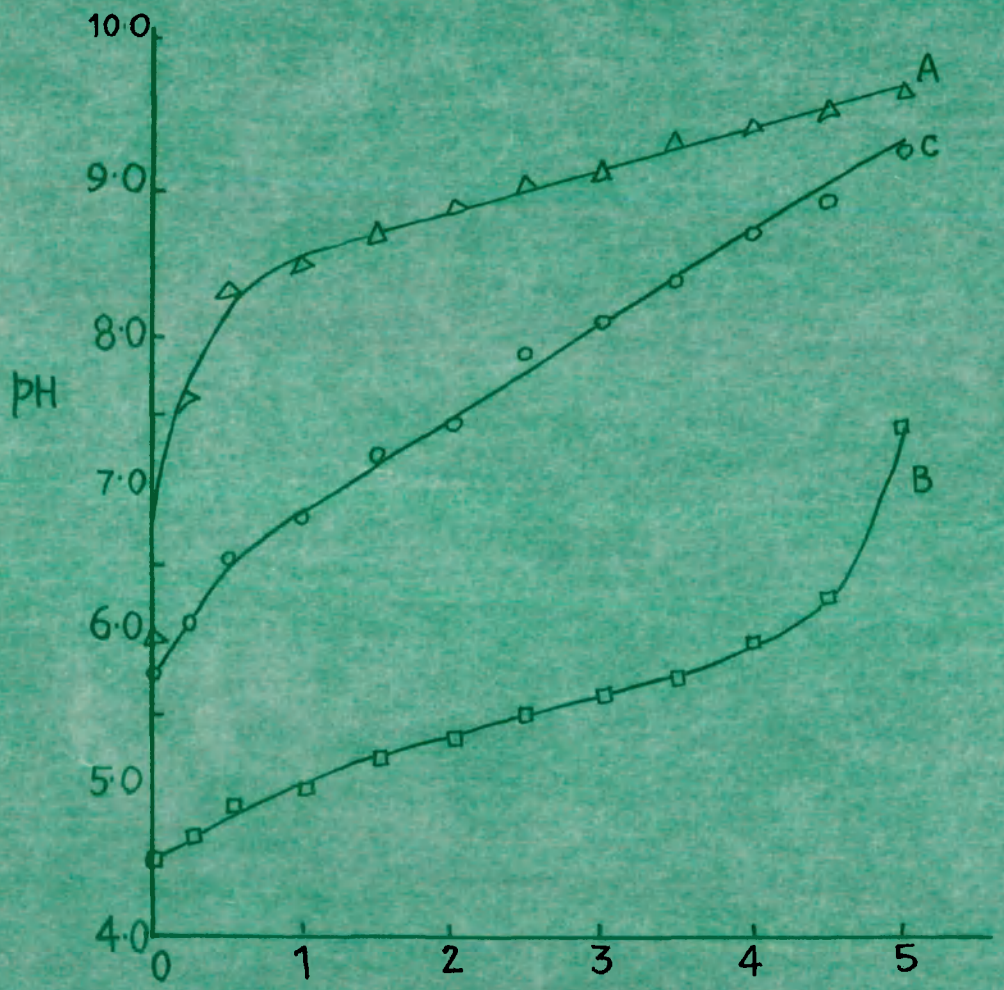
(B) = 50 ml of 0.005M Titanous Chloride(in the cell)

(C) = 25 ml of 0.02M L-Leucine + 25 ml of 0.01M Titanous Chloride (in the cell).

(Vide Fig. No.18 B)

FIGURE NO. 19B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL-α-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02M DL-α-ALANINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO. 19B

T A B L E No.19 B

pH-metric titrations of Ti(III)-∝-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	4.50	5.78
0.25	7.60	4.65	6.18
0.50	8.30	4.85	6.52
1.00	8.50	5.00	6.80
1.50	8.70	5.20	7.25
2.00	8.90	5.30	7.45
2.50	9.05	5.50	7.85
3.00	9.15	5.60	8.10
3.50	9.30	5.70	8.35
4.00	9.40	5.95	8.70
4.50	9.50	6.25	8.90
5.00	9.60	7.40	9.25

(A) = 50 ml of 0.01M DL-∝-Alanine (in the cell)

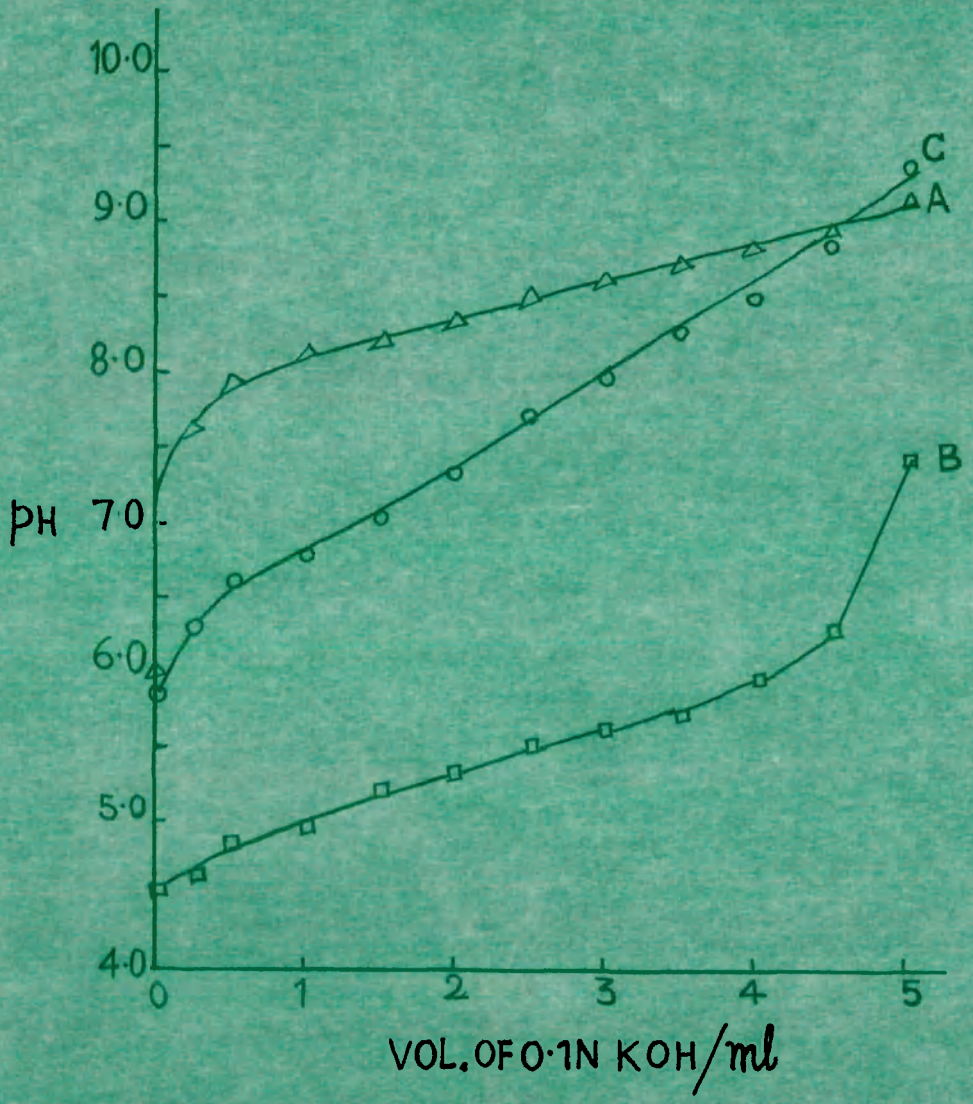
(B) = 50 ml of 0.005M Titanous Chloride (in the cell)

(C) = 25 ml of 0.02M DL - ∝-Alanine + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.19 B)

FIGURE NO. 20B

pH-METRIC TITRATIONS



A = 50 ml. OF 0·01M DL-VALINE (IN THE CELL)

B = 50 ml OF 0·005M $TiCl_3$ (IN THE CELL)

C = 25 ml OF 0·02 M DL-VALINE + 25 ml OF 0·01M $TiCl_3$ (IN THE CELL)

VIDE TABLE NO. 20B

T A B L E No.20 B

pH-metric titrations of Ti(III)-DL-Valine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	4.50	5.88
0.25	7.60	4.65	6.28
0.50	7.90	4.85	6.62
1.00	8.10	4.95	6.75
1.50	8.20	5.20	7.08
2.00	8.30	5.30	7.38
2.50	8.50	5.50	7.70
3.00	8.60	5.60	7.95
3.50	8.70	5.70	8.25
4.00	8.80	5.95	8.50
4.50	8.90	6.25	8.85
5.00	9.10	7.40	9.35

(A) = 50 ml of 0.01M DL-Valine (in the cell)

(B) = 50 ml of 0.005M Titanous Chloride (in the cell)

(C) = 25 ml of 0.02M DL-Valine + 25 ml of 0.01M Titanous Chloride (in the cell)

(Vide Fig. No.20 B)

T A B L E No.13 C

pH-metric titration of Glycine (0.01M ; pK_a = 9.77) and Titanous Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.30	0.10	-5.4772	4.5156	xx
0.50	6.60	0.20	-5.2158	4.6043	xx
1.00	6.85	0.40	-5.0145	4.8245	xx
1.50	7.20	0.57	-4.7115	4.8743	xx
2.00	7.40	0.74	-4.5808	xx	xx
2.50	7.65	0.93	-4.4008	xx	xx
3.00	7.90	1.11	-4.2315	xx	xx
3.50	8.20	1.26	-4.0312	xx	3.8366
4.00	8.50	1.42	-3.8565	xx	3.8245
4.50	8.80	1.56	-3.7285	xx	3.8154
5.00	9.15	1.81	-3.6609	xx	xx

Mean log K' = 4.70

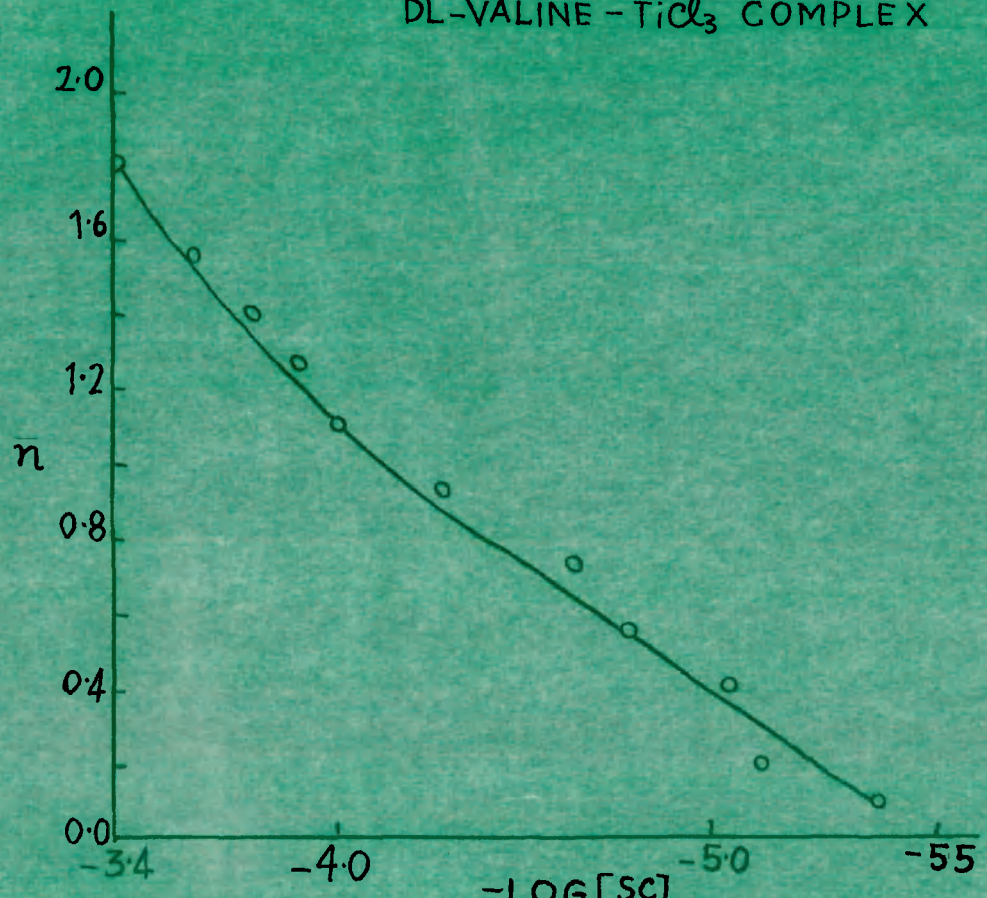
Mean log K" = 3.82

$\log K_s$ = 4.70 + 3.82 = 8.52 Calculated

$\log K_s$ = 8.50 Graphically.

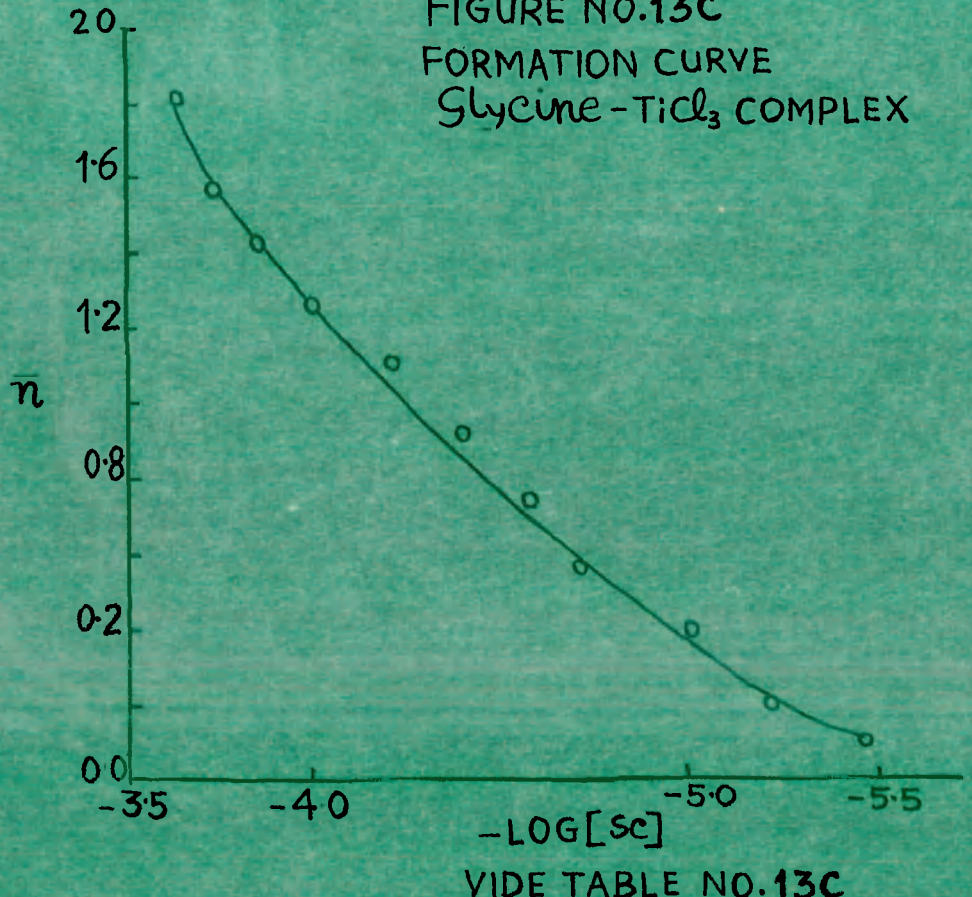
(Vide Fig. No.13 C)

FIGURE NO.20C
FORMATION CURVE
DL-VALINE - $TiCl_3$ COMPLEX



VIDE TABLE NO.20C

FIGURE NO.13C
FORMATION CURVE
Glycine - $TiCl_3$ COMPLEX



VIDE TABLE NO.13C

T A B L E No.14 C

pH-metric titration of DL-Serine (0.01M ; pK_a = 9.15) and Titanous Chloride(0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.60	xx	xx	xx	xx
0.25	5.90	0.10	-5.2522	4.2956	xx
0.50	6.40	0.20	-4.7958	4.2983	xx
1.00	6.70	0.40	-4.4555	4.3542	xx
1.50	7.10	0.57	-4.1995	4.3593	xx
2.00	7.35	0.74	-4.0108	xx	xx
2.50	7.65	0.93	-3.8308	xx	xx
3.00	7.85	1.11	-3.6615	xx	xx
3.50	8.10	1.26	-3.5112	xx	3.3177
4.00	8.40	1.42	-3.3365	xx	3.3045
4.50	8.80	1.56	-3.1095	xx	3.2154
5.00	9.15	1.81	-3.0410	xx	xx

Mean log K' = 4.33

Mean log K" = 3.27

Log K_s = 4.33 + 3.27 = 7.60 Calculated

log K_s = 7.60 Graphically.

(Vide Fig. No.14 C)

T A B L E No.15 C

pH-metric titration of L-Asparagine (0.01M ; pK_a = 8.85) and Titanous Chloride(0.055M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.55	xx	xx	xx	xx
0.25	5.80	0.10	-5.0522	4.0956	xx
0.50	6.25	0.20	-4.6458	4.1343	xx
1.00	6.50	0.40	-4.4445	4.2542	xx
1.50	6.80	0.57	-4.1995	4.2623	xx
2.00	7.20	0.74	-3.8608	xx	xx
2.50	7.50	0.93	-3.6308	xx	xx
3.00	7.70	1.11	-3.5115	xx	xx
3.50	8.00	1.26	-3.3112	xx	3.1276
4.00	8.30	1.42	-3.0865	xx	3.0543
4.50	8.65	1.56	-2.9585	xx	3.0451
5.00	9.00	1.81	-2.8910	xx	xx

Mean log K' = 4.18

Mean log K" = 3.07

$\log K_s$ = 4.18 + 3.07 = 7.25 Calculated

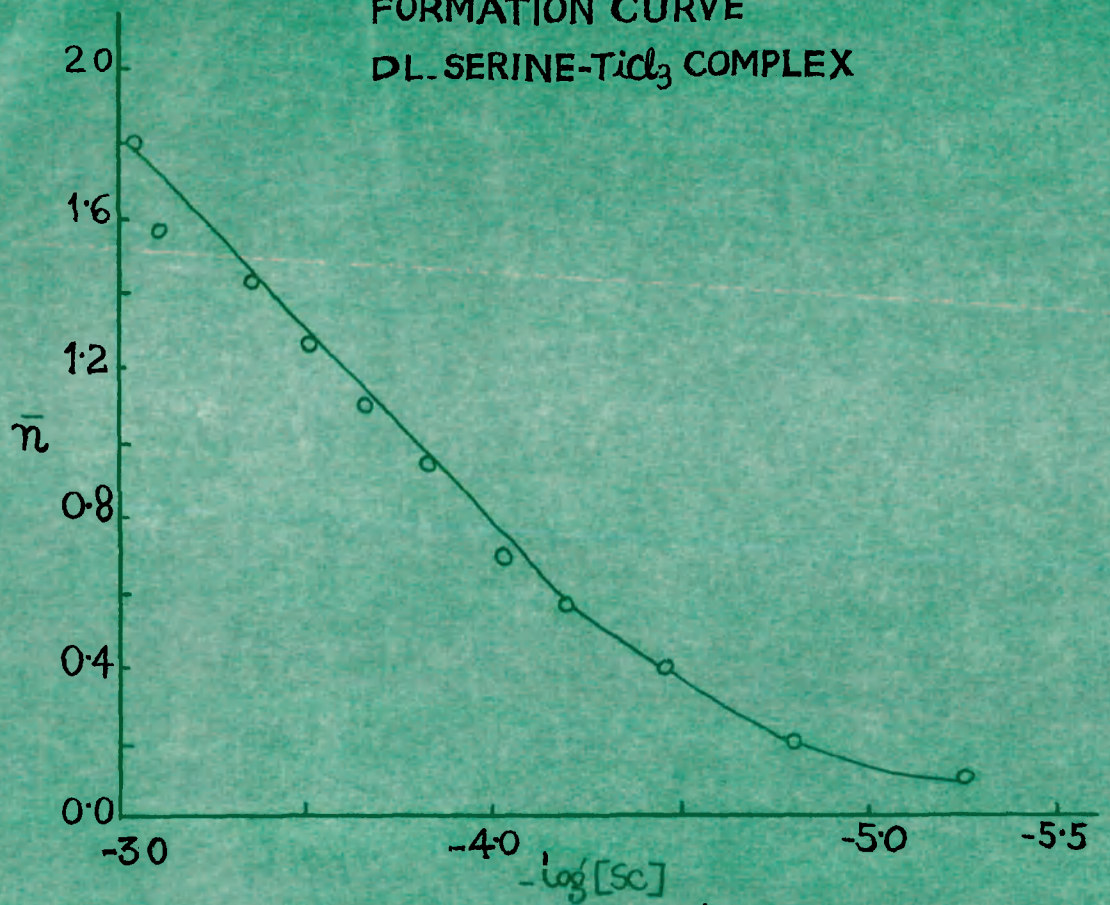
$\log K_s$ = 7.20 Graphically.

(Vide Fig. No.15 C)

FIGURE NO. 14C

FORMATION CURVE

DL-SERINE-$TiCl_3$ COMPLEX

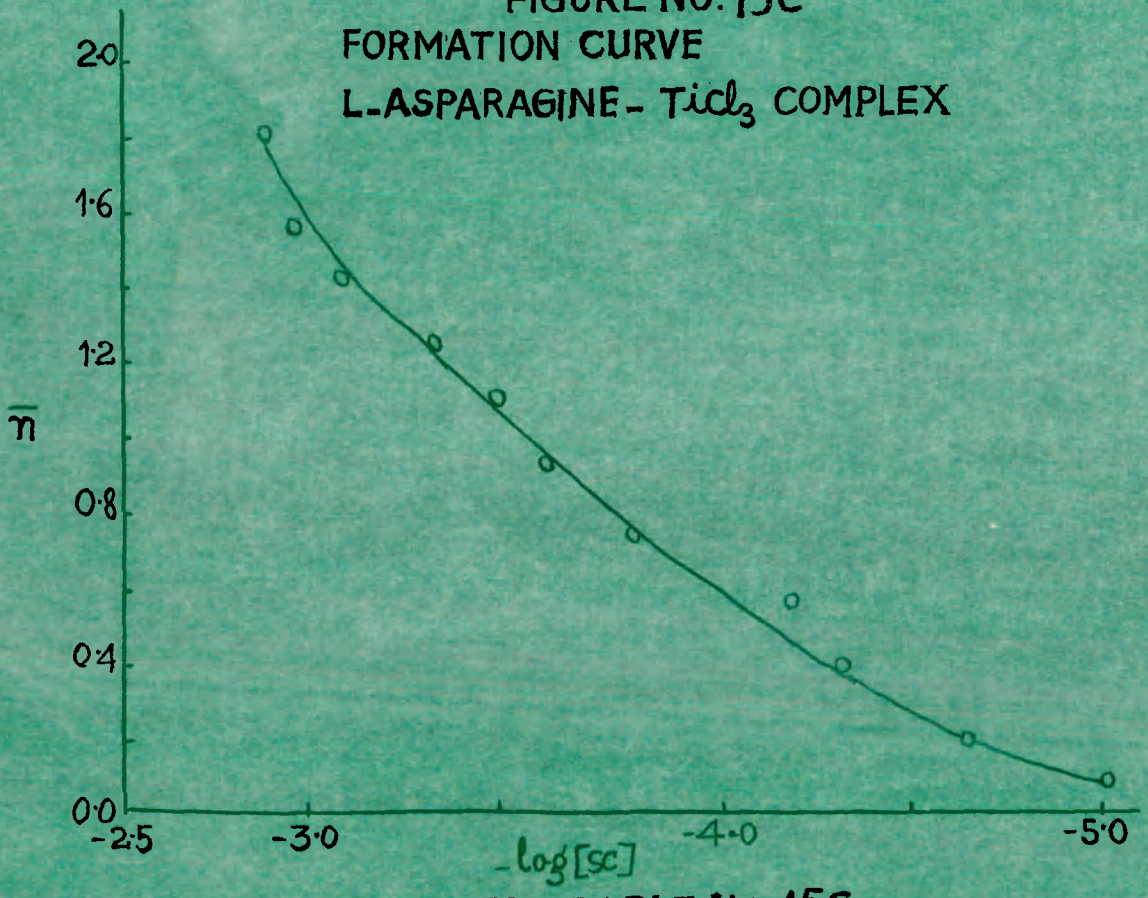


VIDE TABLE NO. 14C

FIGURE NO. 15C

FORMATION CURVE

L-ASPARAGINE- $TiCl_3$ COMPLEX



VIDE TABLE NO. 15C

T A B L E No.16 C

pH-metric titration of β-Alanine (0.01M ; pK_a = 9.87) and Titanous Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.70	xx	xx	xx	xx
0.25	6.20	0.10	-6.1122	5.1559	xx
0.50	6.50	0.20	-5.9058	5.1943	xx
1.00	6.80	0.40	-5.6545	5.4642	xx
1.50	7.20	0.57	-5.3095	5.4723	xx
2.00	7.45	0.74	-5.1208	xx	xx
2.50	7.75	0.93	-4.8908	xx	xx
3.00	7.95	1.11	-4.7715	xx	xx
3.50	8.20	1.26	-4.6212	xx	4.4276
4.00	8.50	1.42	-4.4465	xx	4.4156
4.50	8.85	1.56	-4.2685	xx	3.3954
5.00	9.20	1.81	-4.2010	xx	xx

Mean log K' = 5.31

Mean log K" = 4.41

$\log K_s$ = 5.31 + 4.41 = 9.72 Calculated

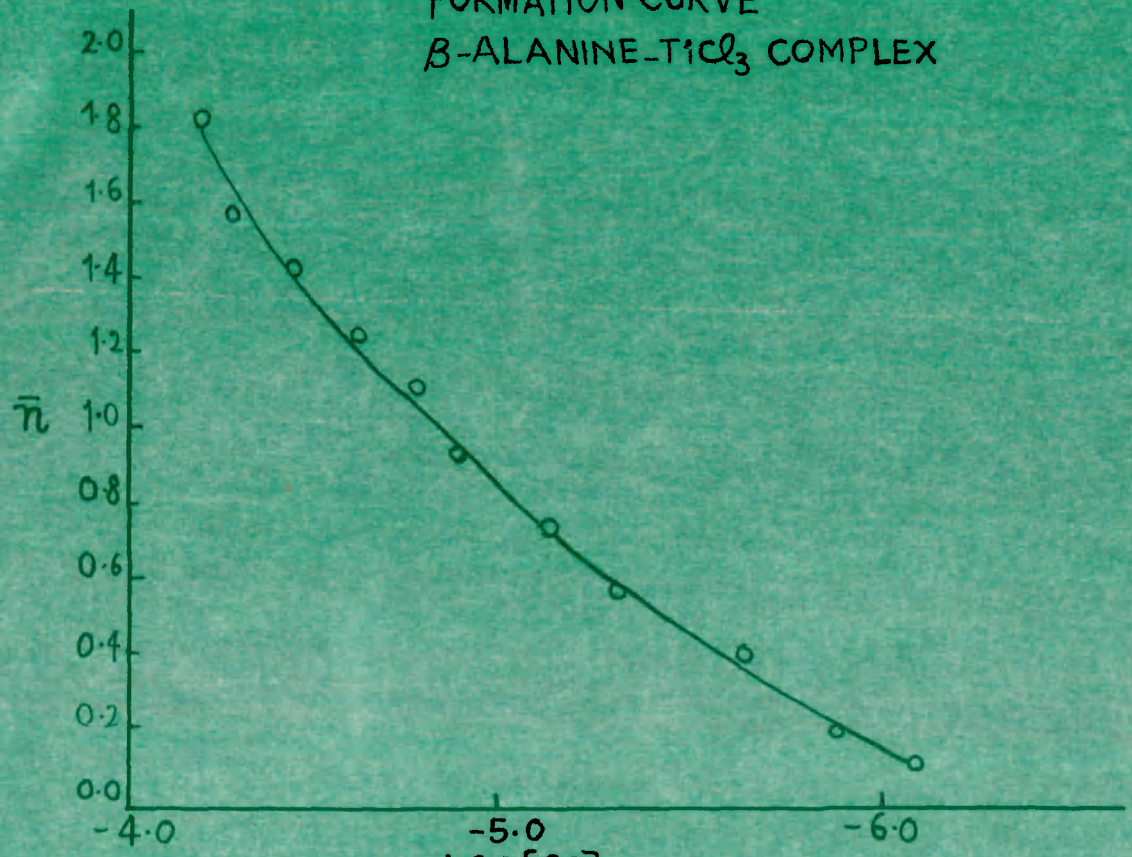
$\log K_s$ = 9.70 Graphically.

(Vide Fig. No.16 C)

FIGURE NO. 16C

FORMATION CURVE

β-ALANINE-$TiCl_3$ COMPLEX

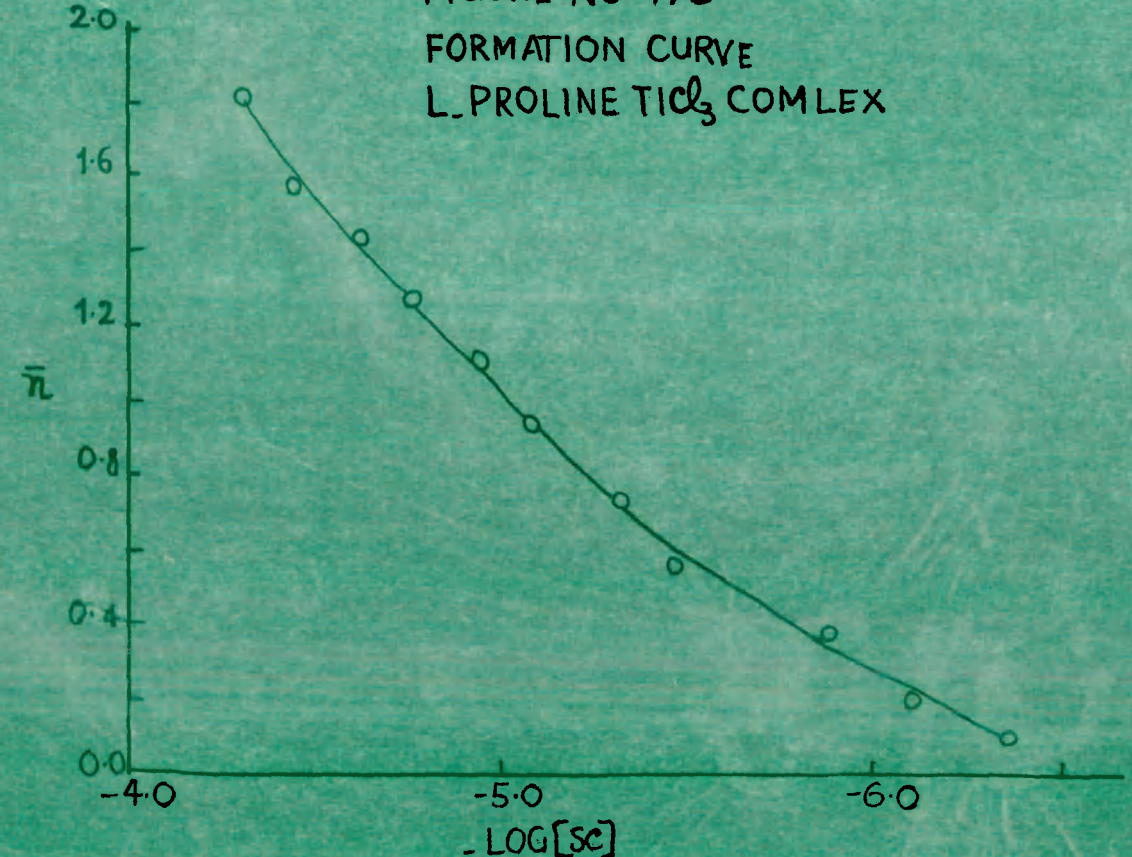


VIDE TABLE NO. 16C

FIGURE NO. 17C

FORMATION CURVE

L-PROLINE $TiCl_3$ COMLEX



VIDE TABLE NO. 17C

T A B L E No.17 C

pH-metric titration of L-Proline (0.01M ; pK_a = 10.60) and Titanous Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.25	0.10	-6.3522	5.4056	xx
0.50	6.55	0.20	-6.0958	5.4843	xx
1.00	6.80	0.40	-5.8955	5.5042	xx
1.50	7.30	0.57	-5.4495	5.5943	xx
2.00	7.50	0.74	-5.3108	xx	xx
2.50	7.80	0.93	-5.0808	xx	xx
3.00	8.00	1.11	-4.9615	xx	xx
3.50	8.30	1.26	-4.7612	xx	4.5676
4.00	8.55	1.42	-4.6365	xx	4.6047
4.50	8.90	1.56	-4.4685	xx	4.6254
5.00	9.30	1.81	-4.3410	xx	xx

Mean log K' = 5.49

Mean log K" = 4.59

$\log K_s$ = 5.49 + 4.59 = 10.08 Calculated

$\log K_s$ = 10.05 Graphically.

(Vide Fig. No.17 C)

T A B L E No.18 C

pH-metric titration of L-Leucine (0.01M ; pK_a = 9.92) and Titanous Chloride (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.34	0.10	-5.5822	4.6256	xx
0.50	6.68	0.20	-5.2858	4.6743	xx
1.00	7.05	0.40	-4.9645	4.7745	xx
1.50	7.32	0.57	-4.7495	4.8123	xx
2.00	7.63	0.74	-4.4008	xx	xx
2.50	7.85	0.93	-4.3508	xx	xx
3.00	8.02	1.11	-4.2615	xx	xx
3.50	8.32	1.26	-4.0812	xx	3.8876
4.00	8.65	1.42	-3.8565	xx	3.8254
4.50	9.05	1.56	-3.6285	xx	3.7854
5.00	9.40	1.81	-3.5609	xx	xx

Mean log K' = 4.72

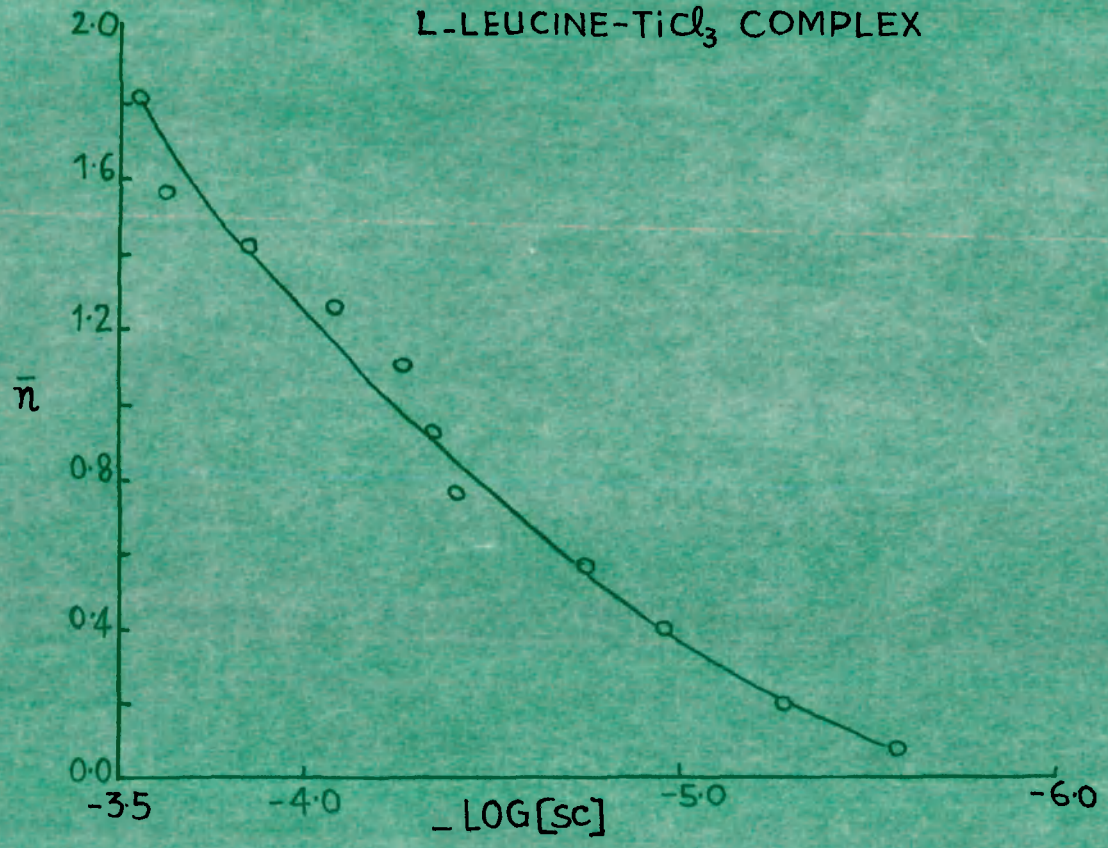
Mean log K" = 3.83

$\log K_s$ = 4.72 + 3.83 = 8.55 Calculated

$\log K_s$ = 8.50 Graphically.

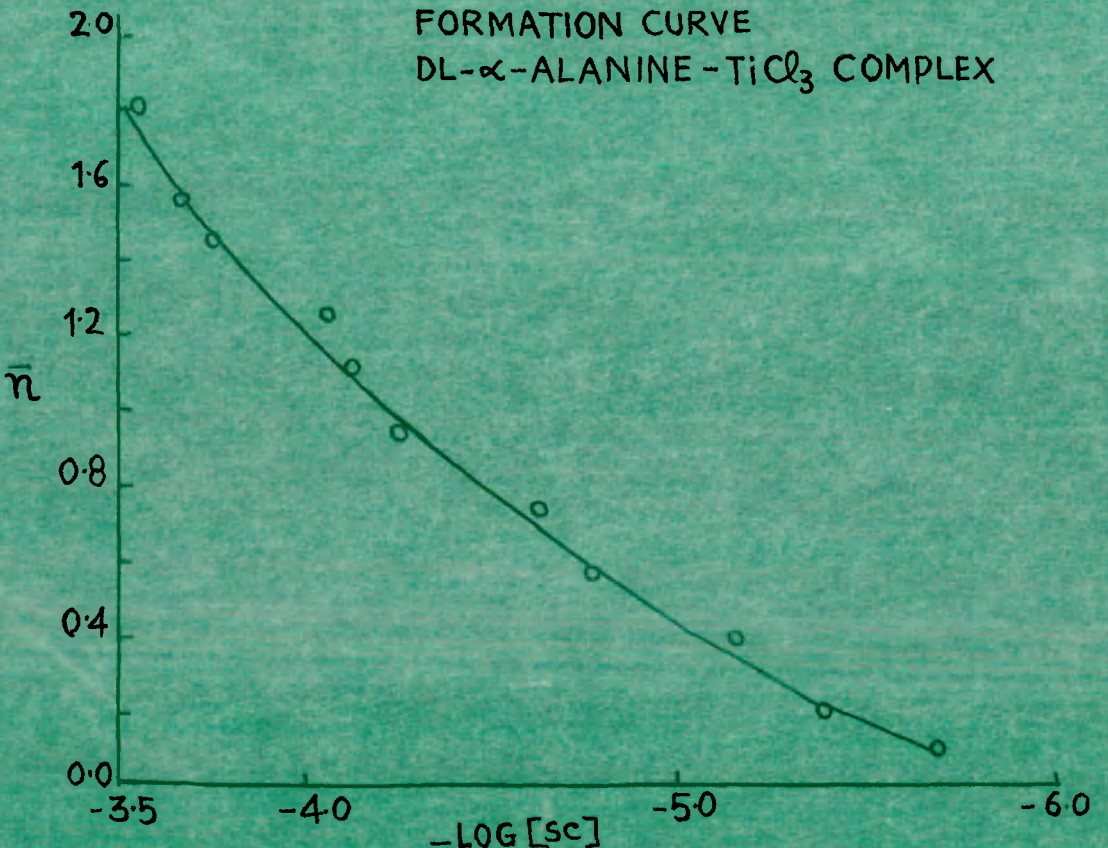
(Vide Fig. No.18 C)

FIGURE NO. 18C
FORMATION CURVE
L-LEUCINE-$TiCl_3$ COMPLEX



VIDE TABLE NO. 18C

FIGURE NO. 19C
FORMATION CURVE
DL-α-ALANINE-$TiCl_3$ COMPLEX



VIDE TABLE NO. 19C

T A B L E No. 19 C

pH-metric titration of DL- α-Alanine (0.01M ; pK_a = 9.86) and Titanous Chloride (0.005M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.78	xx	xx	xx	xx
0.25	6.18	0.10	-5.6822	4.7256	xx
0.50	6.52	0.20	-5.3858	4.7743	xx
1.00	6.80	0.40	-5.1545	4.8645	xx
1.50	7.25	0.57	-4.7515	4.9143	xx
2.00	7.45	0.74	-4.6205	xx	xx
2.50	7.85	0.93	-4.2408	xx	xx
3.00	8.10	1.11	-4.1215	xx	xx
3.50	8.35	1.26	-3.9712	xx	3.7776
4.00	8.70	1.42	-3.7465	xx	3.7155
4.50	8.90	1.56	-3.6685	xx	3.7054
5.00	9.25	1.81	-3.5509	xx	xx

Mean log K' = 4.81

Mean log K" = 3.72

$\log K_s$ = 4.81 + 3.72 = 8.53 Calculated

$\log K_s$ = 8.50 Graphically.

(Vide Fig. No.19 C)

T A B L E No.20 C

pH-metric titration of DL-Valine (0.01M ; pK_a = 9.71) and Titanous Chloride(0.005M); all in 50 ml. $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.88	xx	xx	xx	xx
0.25	6.28	0.10	-5.4322	4.4756	xx
0.50	6.62	0.20	-5.1358	4.5243	xx
1.00	6.75	0.40	-5.0545	4.8645	xx
1.50	7.08	0.57	-4.7795	4.9723	xx
2.00	7.38	0.74	-4.5408	xx	xx
2.50	7.70	0.93	-4.2908	xx	xx
3.00	7.95	1.11	-4.0215	xx	xx
3.50	8.25	1.26	-3.9212	xx	3.4276
4.00	8.50	1.42	-3.7912	xx	3.4745
4.50	8.85	1.56	-3.6185	xx	3.4864
5.00	9.35	1.81	-3.4009	xx	xx

Mean log K' = 4.70

Mean log K" = 3.46

$\log K_s$ = 4.70 + 3.46 = 8.16 Calculated

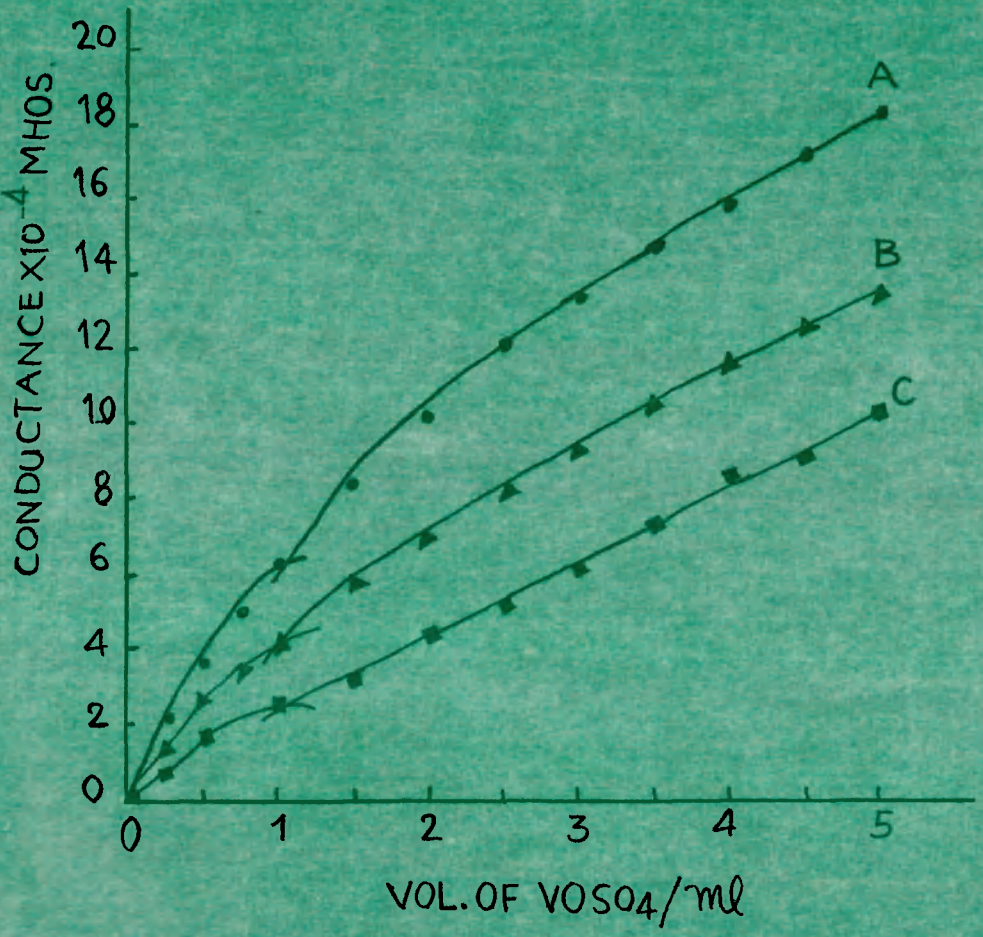
$\log K_s$ = 8.20 Graphically.

(Vide Fig. No.20 C)

FIGURE NO. 21A

REVERSE CONDUCTOMETRIC TITRATIONS.

L-ASPARAGINE-VOSO4



A = 20 ml OF 0·005 M L-ASPARAGINE Vs. 0·1 M VOSO4

B = 20 ml OF 0·0033 ML-ASPARAGINE Vs. 0·066M VOSO4

C = 20 ml OF 0·0025 ML-ASPARAGINE VS. 0·05 M VOSO4

VIDE TABLE NO. 21A

TABLE No.21 A

Conductometric titrations (Reverse)

L-Asparagine - Vanadyl Sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.364	0.303	0.298
0.5	3.70	2.70	1.94
1.0	6.25	4.25	2.63
1.5	8.34	5.96	3.33
2.0	10.30	7.15	4.45
2.5	12.05	8.34	5.05
3.0	13.40	9.54	6.15
3.5	14.90	10.65	7.40
4.0	15.65	11.75	8.70
4.5	17.20	12.65	9.01
5.0	18.30	13.50	10.30

1st.titration :- 20 ml of 0.005M L-Asparagine
Vs. 0.1M Vanadyl Sulphate

2nd.titration :- 20 ml of 0.0033M L-Asparagine
Vs. 0.066M Vanadyl Sulphate

3rd.titration :- 20 ml of 0.0025M L-Asparagine
Vs. 0.05M Vanadyl Sulphate

(Vide Fig. No.21 A)

FIGURE NO. 55A

WIDE TABLE NO. 55A

TABLE No.22 A

Conductometric - Vanadyl Sulphate

β-Alanine - Vanadyl Sulphate

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.22	0.39	0.23
0.5	2.48	3.13	1.96
1.0	3.84	4.76	3.03
1.5	5.13	5.70	3.17
2.0	6.25	6.05	3.50
2.5	6.90	7.15	4.65
3.0	8.34	7.70	4.76
3.5	9.54	8.00	5.00
4.0	10.60	8.35	5.13
4.5	11.00	8.70	5.40
5.0	11.6	0.09	5.55

1st.titration :- 40 ml of 0.005M β-Alanine Vs. 0.1M Vanadyl Sulphate

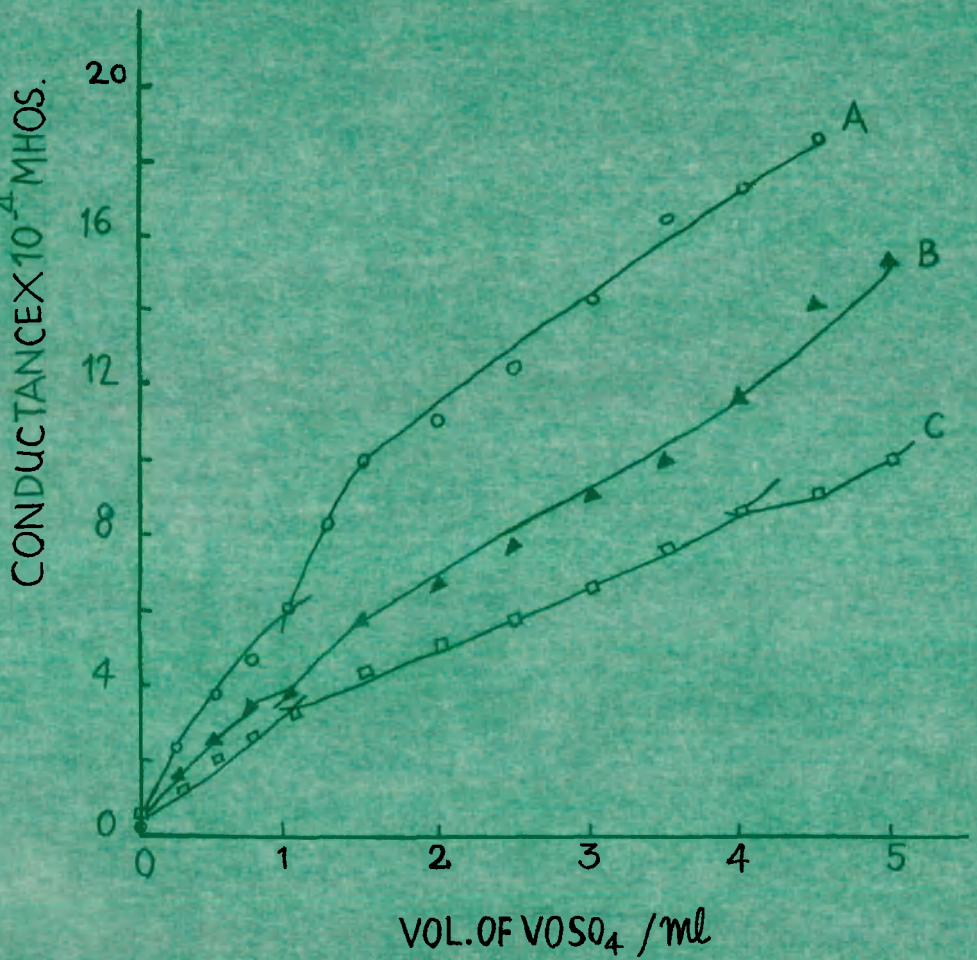
2nd.titration :- 40 ml of 0.0033M β-Alanine Vs. 0.066M Vanadyl Sulphate

3rd.titration :- 40 ml of 0.0025M β-Alanine Vs. 0.05M Vanadyl Sulphate

(Vide Fig. No.22 A)

FIGURE NO. 23A

REVERSE CONDUCTOMETRIC TITRATIONS
DL-SERINE -$VOSO_4$



A = 20 ml OF 0·005 M DL-SERINE VS. 0·1 M $VOSO_4$

B = 20 ml OF 0·0033 M DL-SERINE VS. 0·066 M $VOSO_4$

C = 20 ml OF 0·002 M DL-SERINE VS. 0·04 M $VOSO_4$

VIDE TABLE NO. 23A

T A B L E No.23 A

Conductometric titrations (Reverse)

DL-Serine - Vanadyl Sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titrations. Conductance $x10^{-4}$mhos.	3rd.titration. Conductence $x10^{-4}$mhos-
0.0	0.286	0.227	0.40
0.5	3.84	2.63	2.08
1.0	6.05	3.84	3.34
1.5	8.25	5.88	4.55
2.0	10.00	6.65	5.13
2.5	11.10	7.70	5.88
3.0	12.50	0.09	6.66
3.5	14.30	10.00	7.70
4.0	16.60	11.80	8.70
4.5	17.20	14.25	9.09
5.00	18.50	15.40	10.00

1st.titration :- 20 ml of 0.005M DL-Serine
Vs. 0.1M Vanadyl Sulphate

2nd.titration :- 20 ml of 0.0033M DL-Serine
Vs. 0.066M Vanadyl Sulphate

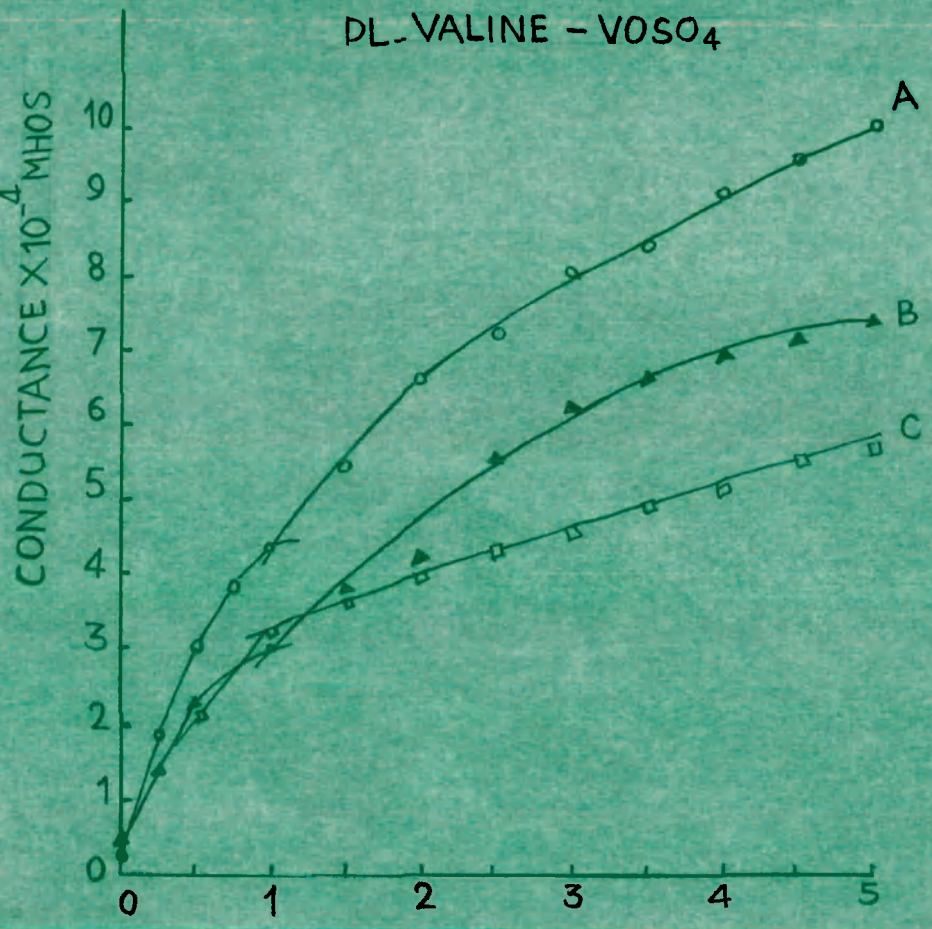
3rd.titration :- 20 ml of 0.002M DL-Serine
Vs. 0.04M Vanadyl Sulphate

(Vide Fig. No. 23 A)

FIGURE NO. 24A

REVERSE CONDUCTOMETRIC TITRATIONS.

DL-VALINE – $VOSO_4$



A = 20 ml OF 0·055 M DL-VALINE Vs. 0·1M $VOSO_4$

B = 20 ml OF 0·0033 M DL-VALINE VS. 0·066M $VOSO_4$

C = 20 ml OF 0·0025 M DL-VALINE Vs. 0·05 M $VOSO_4$.

VIDE TABLE NO. 24A

T A B L E No.24 A

Conductometric-titrations (Reverse)

DL-Valine - Vanadyl Sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.00	0.40	0.32	0.24
0.5	3.08	2.38	2.17
1.0	4.45	3.03	3.12
1.5	5.55	3.84	3.84
2.0	6.66	4.15	4.00
2.5	7.15	5.55	4.25
3.0	8.00	6.25	4.55
3.5	8.35	6.66	4.88
4.0	9.09	6.90	5.13
4.5	9.55	7.15	5.55
5.0	10.00	7.40	5.70

1st.titration :- 20 ml of 0.005M DL-Valine
Vs. 0.1M Vanadyl Sulphate

2nd.titration :- 20 ml of 0.0033M DL-Valine
Vs. 0.066M Vanadyl Sulphate

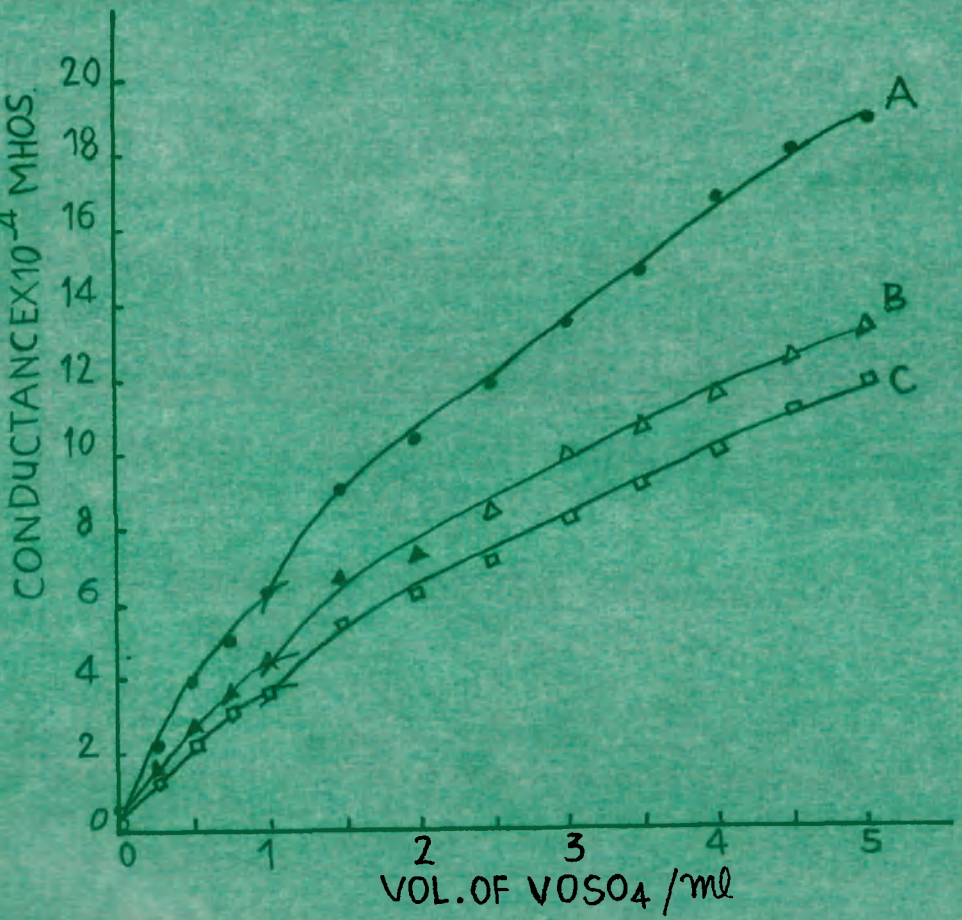
3rd.titration :- 20 ml of 0.0025M DL-Valine
Vs. 0.05M Vanadyl Sulphate

(Vide Fig. No.24 A)

FIGURE NO. 25A

REVERSE CONDUCTOMETRIC TITRATIONS

L-PROLINE-$VOSO_4$



A = 20 ml OF 0·005 M L-PROLINE Vs. 0·1 M $VOSO_4$

B = 20 ml OF 0·0033 M L-PROLINE Vs. 0·066 M $VOSO_4$

C = 20 ml OF 0·0025 M L-PROLINE Vs. 0·05 M $VOSO_4$

VIDE TABLE NO. 25A

TABLE No.25 A

Conductometric titrations (Reverse)

L - Proline-Vanadyl Sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.41	0.37	0.35
0.5	4.08	2.86	2.27
1.0	6.45	4.55	3.85
1.5	9.09	6.66	5.55
2.0	10.40	7.40	6.25
2.5	11.90	8.34	7.14
3.0	13.50	10.00	8.33
3.5	14.90	10.50	9.09
4.0	16.40	11.70	10.00
4.5	18.00	12.50	11.10
5.0	18.80	13.30	11.90

1st.titration :- 20 ml of 0.005M L- Proline
Vs. 0.1M Vanadyl Sulphate

2nd.titration :- 20 ml of 0.0033M L-Proline
Vs. 0.066M Vanadyl Sulphate

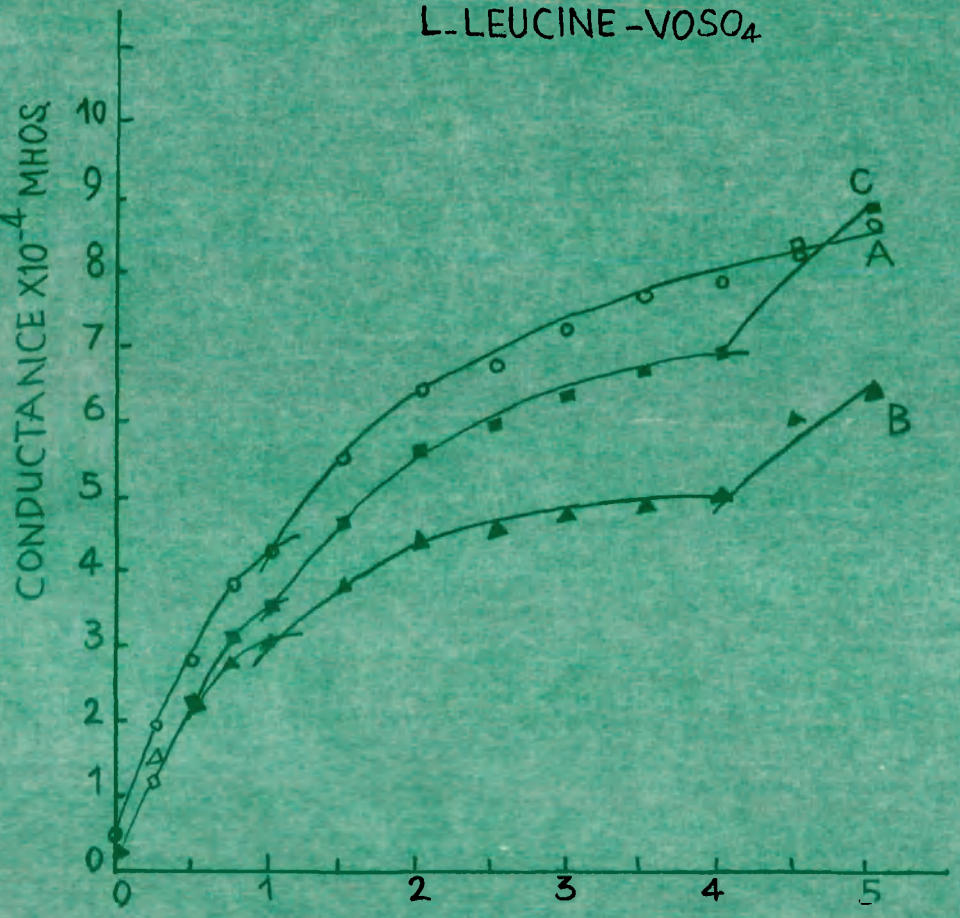
3rd.titration :- 20 ml of 0.0025M L-Proline
Vs. 0.05M Vanadyl Sulphate

(Vide Fig. No.25 A)

FIGURE NO. 26A

REVERSE CONDUCTOMETRIC TITRATIONS

L-LEUCINE - $VOSO_4$



VOL. OF VOSO4 / ml

A = 20 ml OF 0·005M L-LEUCINE Vs. 0·1M $VOSO_4$

B = 20 ml OF 0·0033M L-LEUCINE Vs. 0·066M $VOSO_4$

C = 20 ml OF 0·0025M L-LEUCINE Vs. 0·05M $VOSO_4$

VIDE TABLE NO. 26A

T A B L E No.26 A

Conductometric - titrations (Reverse)

L-Leucine-Vanadyl Sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration.Con - ductance $x10^{-4}$mhos.
0.0	0.40	0.29	0.25
0.5	2.85	2.22	2.00
1.0	4.25	3.12	3.00
1.5	5.55	3.88	3.50
2.0	6.45	4.45	4.75
2.5	6.66	4.54	5.55
3.0	7.15	4.65	5.88
3.5	7.77	4.88	6.25
4.0	7.80	5.00	6.66
4.5	8.34	6.05	6.90
5.0	8.70	6.45	7.25

1st.titration :- 20 ml of 0.005M L- Leucine
Vs. 0.1M Vanadyl Sulphate

2nd.titration :- 20 ml of 0.0033M L-Leucine
Vs. 0.066M Vanadyl Sulphate

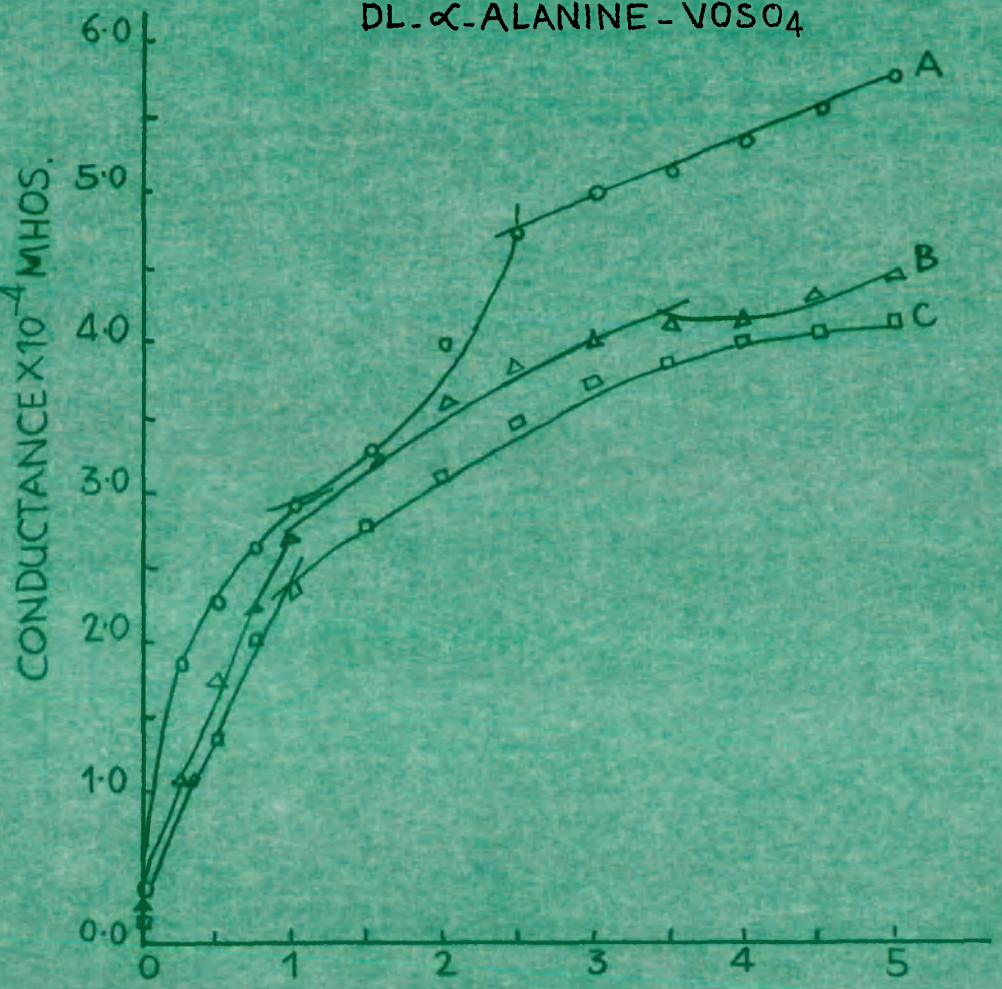
3rd.titration :- 20 ml of 0.0025M L-Leucine
Vs. 0.05M Vanadyl Sulphate

(Vide Fig. No.26 A)

FIGURE NO. 27A

REVERSE CONDUCTOMETRIC TITRATIONS.

DL-α-ALANINE - $VOSO_4$



VOL. OF $VOSO_4$ / ml

A = 20 ml OF 0·005 M DL-α-ALANINE Vs. 0·1M $VOSO_4$

B = 20 ml OF 0·0033 M DL-α-ALANINE Vs. 0·066 M $VOSO_4$

C = 20 ml OF 0·0025 M DL-α-ALANINE Vs. 0·05 M $VOSO_4$

VIDE TABLE NO. 27A

T A B L E No.27 A

Conductometric - titrations (Reverse)

DL- ∝-Alanine-Vanadyl sulphate Complex

Vol.of $VOSO_4$ added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.32	23	0.22
0.5	2.27	1.75	1.63
1.0	2.94	2.70	2.35
1.5	3.33	3.30	2.78
2.0	4.00	3.63	3.12
2.5	4.76	3.88	3.45
3.0	5.00	4.00	3.70
3.5	5.13	4.15	3.84
4.0	5.26	4.15	4.00
4.5	5.55	4.35	4.08
5.0	5.71	4.45	4.16

1st.titration :- 20 ml of 0.005M DL- ∝-Alanine Vs. 0.1M Vanadyl sulphate

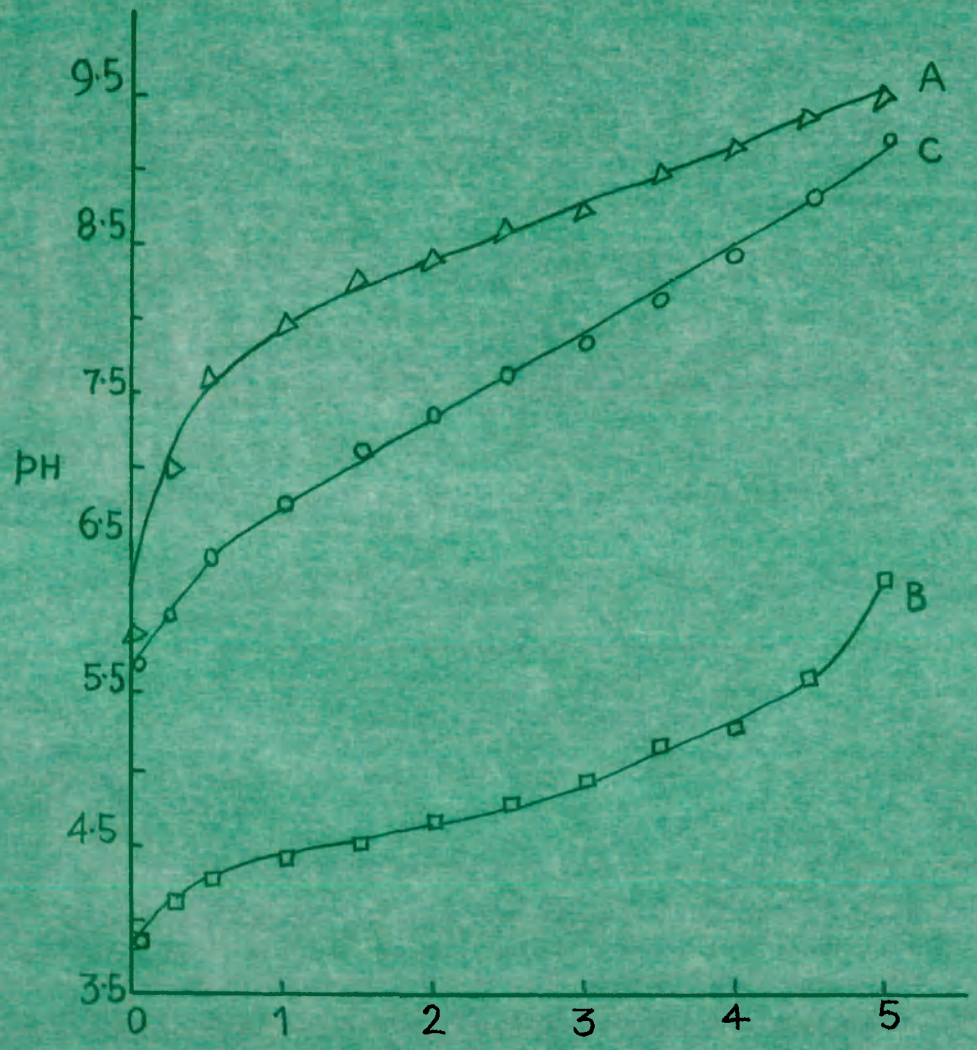
2nd.titration :- 20 ml of 0.0033M DL- ∝-Alanine Vs. 0.066M Vanadyl sulphate

3rd.titration :- 20 ml of 0.0025M DL- ∝-Alanine Vs. 0.05M Vanadyl sulphate

(Vide Fig. No.27 A)

FIGURE NO. 21B

PH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-ASPARAGINE (IN THE CELL)

B = 50 ml OF 0·005 M VOSO4 (IN THE CELL)

C = 25 ml OF 0·02 M L-ASPARAGINE + 25 ml OF 0·01M VOSO4 (IN THE CELL)

VIDE TABLE NO. 21B

T A B L E No.21 B

pH-metric titrations of VO^{2+}-L-Asparagine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	3.85	5.70
0.25	7.00	4.10	6.00
0.50	7.60	4.25	6.40
1.00	7.95	4.40	6.75
1.50	8.25	4.50	7.10
2.00	8.40	4.65	7.35
2.50	8.60	4.75	7.60
3.00	8.70	4.90	7.80
3.50	8.95	5.00	8.10
4.00	9.15	5.25	8.40
4.50	9.30	5.60	8.80
5.00	9.45	6.25	9.20

(A) = 50 ml of 0.01M L-Asparagine (in the cell)

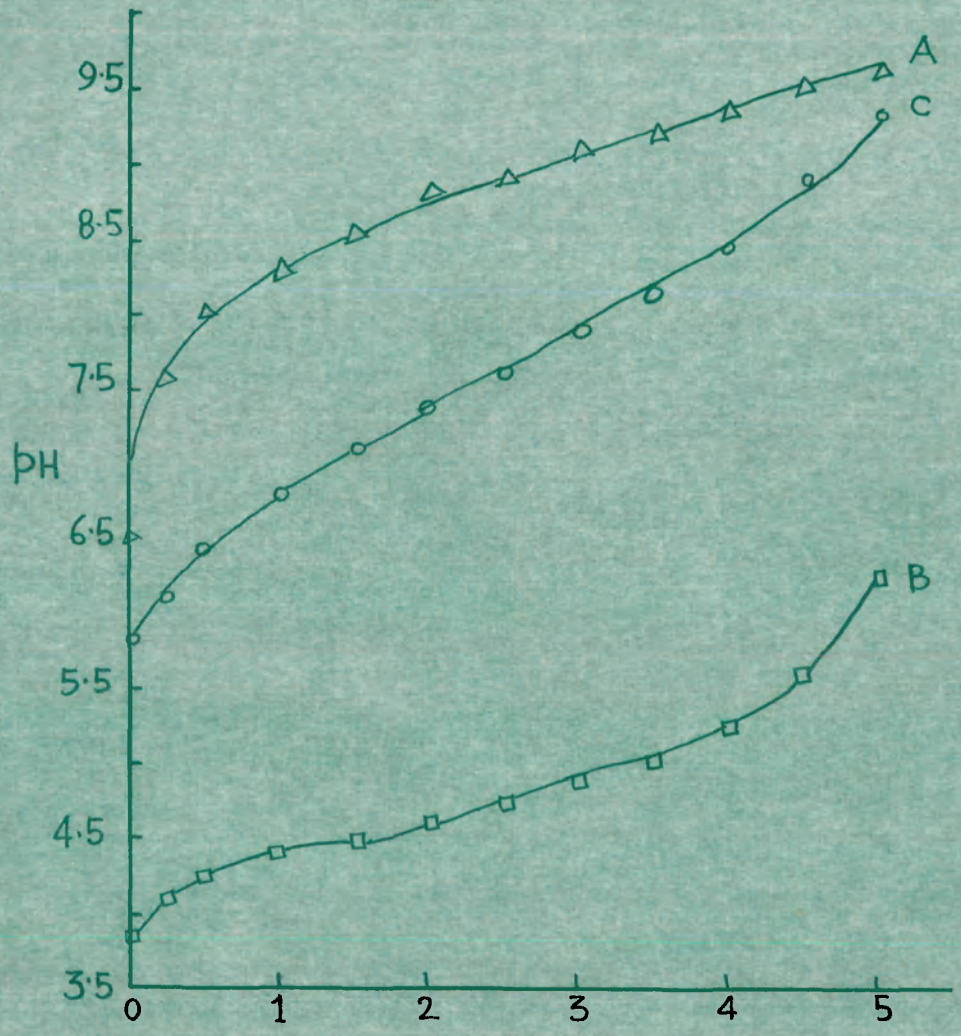
(B) = 50 ml of 0.005M Vanadylsulphate (in the cell)

(C) = 25 ml of 0.02M L-Asparagine + 25 ml of 0.01M Vanadylsulphate (in the cell)

(Vide Fig. No.21 B)

FIGURE NO. 22B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M β-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $VOSO_4$ (IN THE CELL)

C = 25 ml OF 0·02M β-ALANINE + 25 ml OF 0·01M $VOSO_4$ (IN THE CELL)

VIDE TABLE NO. 22B

T A B L E No.22 B

pH-metric titrations of VO^{2+} - β-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.85	5.80
0.25	7.60	4.10	6.15
0.50	8.05	4.25	6.45
1.00	8.30	4.40	6.80
1.50	8.55	4.50	7.15
2.00	8.80	4.65	7.40
2.50	8.90	4.75	7.65
3.00	9.10	4.90	7.90
3.50	9.20	5.00	8.15
4.00	9.40	5.25	8.45
4.50	9.50	5.60	8.90
5.00	9.60	6.25	9.35

(A) = 50 ml of 0.01M β-Alanine (in the cell)

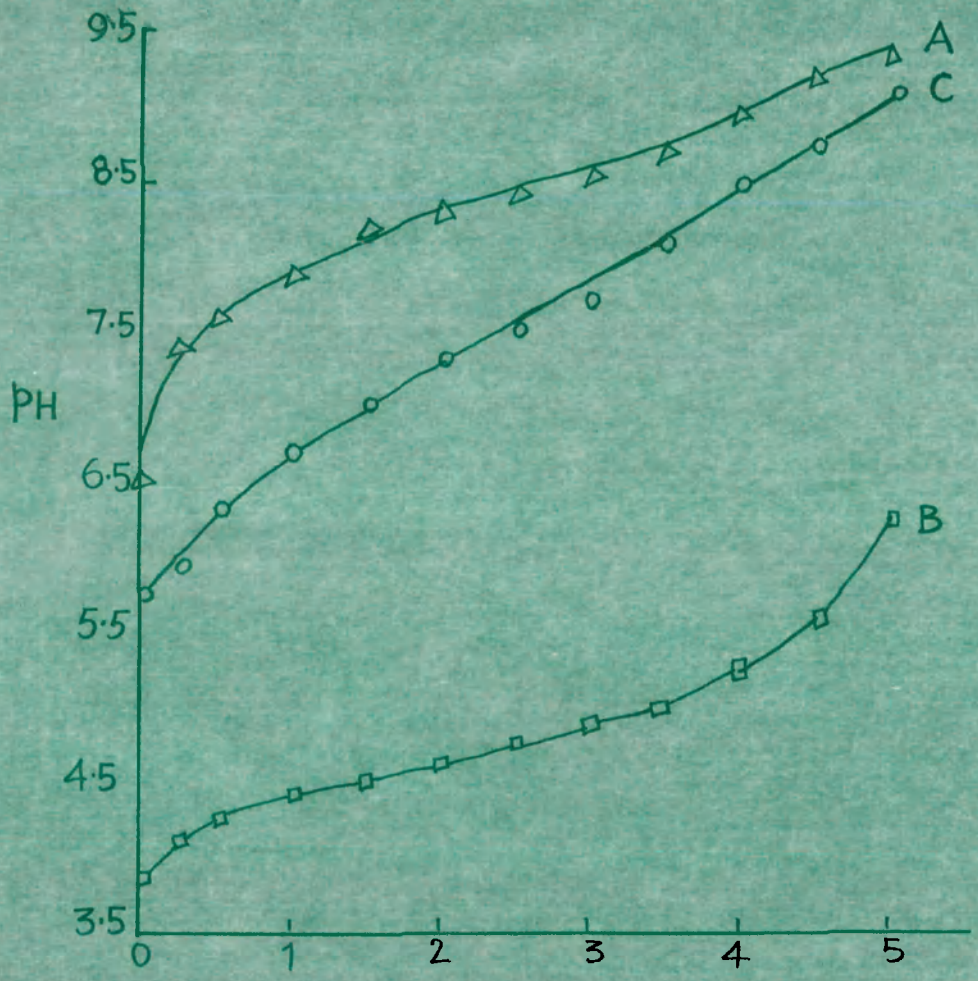
(B) = 50 ml of 0.005M Vanadyl Sulphate (in the cell)

(C) = 25 ml of 0.02M β-Alanine + 25 ml of 0.01M Vanadyl Sulphate (in the cell)

(Vide Fig. No.22 B)

FIGURE NO. 23B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL-SERINE (IN THE CELL)
B = 50 ml OF 0·005M $VOSO_4$ (IN THE CELL)
C = 25 ml OF 0·02 M DL-SERINE + 25 ml OF 0·01M $VOSO_4$

VIDE TABLE NO. 23B

T A B L E No.23 B

pH-metric titrations of VO^{2+} -DL-Serine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.85	5.75
0.25	7.40	4.10	5.95
0.50	7.60	4.25	6.35
1.00	7.90	4.40	6.70
1.50	8.20	4.50	7.05
2.00	8.30	4.65	7.30
2.50	8.40	4.75	7.50
3.00	8.50	4.90	7.70
3.50	8.70	5.00	8.10
4.00	8.95	5.25	8.50
4.50	9.20	5.60	8.75
5.00	9.30	6.25	9.15

(A) = 50 ml of 0.01M DL-Serine (in the cell)

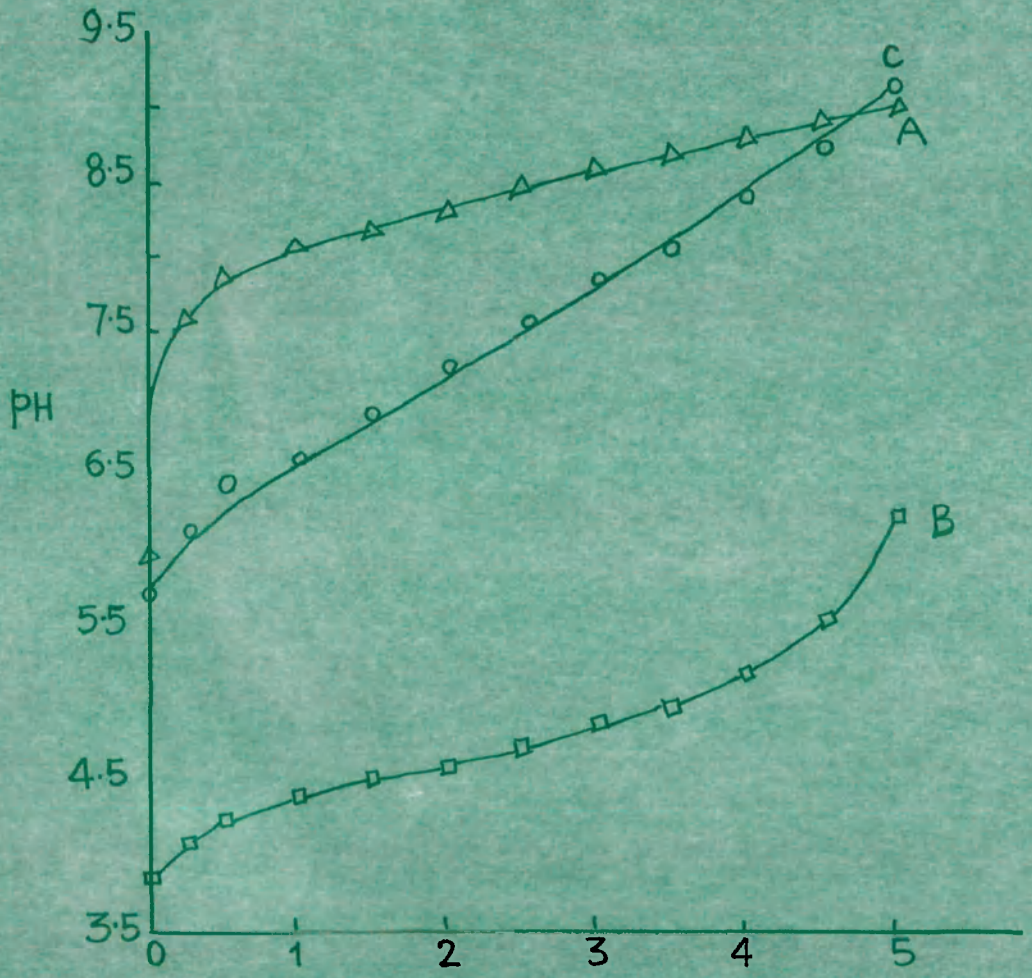
(B) = 50 ml of 0.005M Vanadyl Sulphate(in the cell)

(C) = 25 ml of 0.02M DL-Serine + 25 ml of 0.01M Vanadyl Sulphate (in the cell)

(Vide Fig. No.23 B)

FIGURE NO. 24B

pH-METRIC TITRATIONS.



A = 50 ml OF 0·01M DL-VALINE (IN THE CELL)

B = 50 ml OF 0·005M $VOSO_4$ (IN THE CELL)

C = 25 ml OF 0·02M DL-VALINE + 25 ml OF 0·01M $VOSO_4$ (IN THE CELL)

VIDE TABLE NO. 24B

T A B L E No.24 B

pH-metric titrations of VO^{2+} -DL-valine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	3.85	5.75
0.25	7.60	4.10	6.20
0.50	7.90	4.25	6.55
1.00	8.10	4.40	6.65
1.50	8.20	4.50	7.00
2.00	8.30	4.60	7.30
2.50	8.50	4.75	7.60
3.00	8.60	4.90	7.85
3.50	8.70	5.00	8.05
4.00	8.80	5.25	8.40
4.50	8.90	5.60	8.75
5.00	9.05	6.25	9.40

(A) = 50 ml of 0.01M DL-Valine (in the cell)

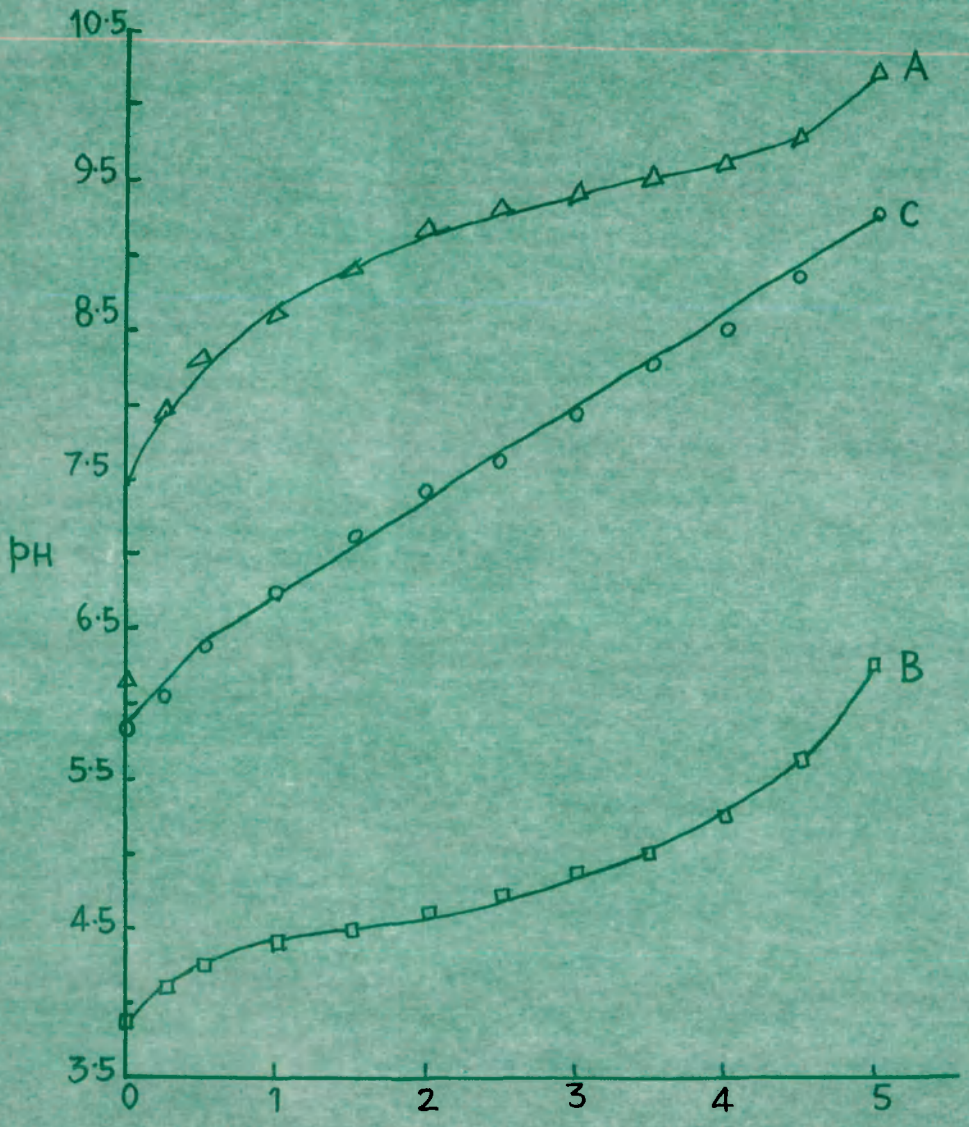
(B) = 50 ml of 0.005M Vanadyl Sulphate(in the cell)

(C) = 25 ml of 0.02M DL-Valine + 25 ml of 0.01M Vanadyl Sulphate (in the cell)

(Vide Fig. No.24 B)

FIGURE NO. 25B

pH-METRIC TITRATIONS.



A=50 ml OF 0·01M L-PROLINE (IN THE CELL)

B=50 ml OF 0·005M $VOSO_4$ (IN THE CELL)

C=25 ml OF 0·02M L-PROLINE + 25 ml OF 0·01M $VOSO_4$ (IN THE CELL)

VIDE TABLE NO. 25B

T A B L E No.25 B

pH-metric titrations of VO^{2+}-L-Proline system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.15	3.85	5.85
0.25	7.95	4.10	6.05
0.50	8.30	4.25	6.40
1.00	8.60	4.40	6.75
1.50	8.90	4.50	7.10
2.00	9.20	4.60	7.45
2.50	9.30	4.75	7.65
3.00	9.40	4.90	7.95
3.50	9.50	5.00	8.25
4.00	9.60	5.25	8.30
4.50	9.80	5.60	8.85
5.00	9.95	6.25	9.25

(A) = 50 ml of 0.01M L-Proline (in the cell)

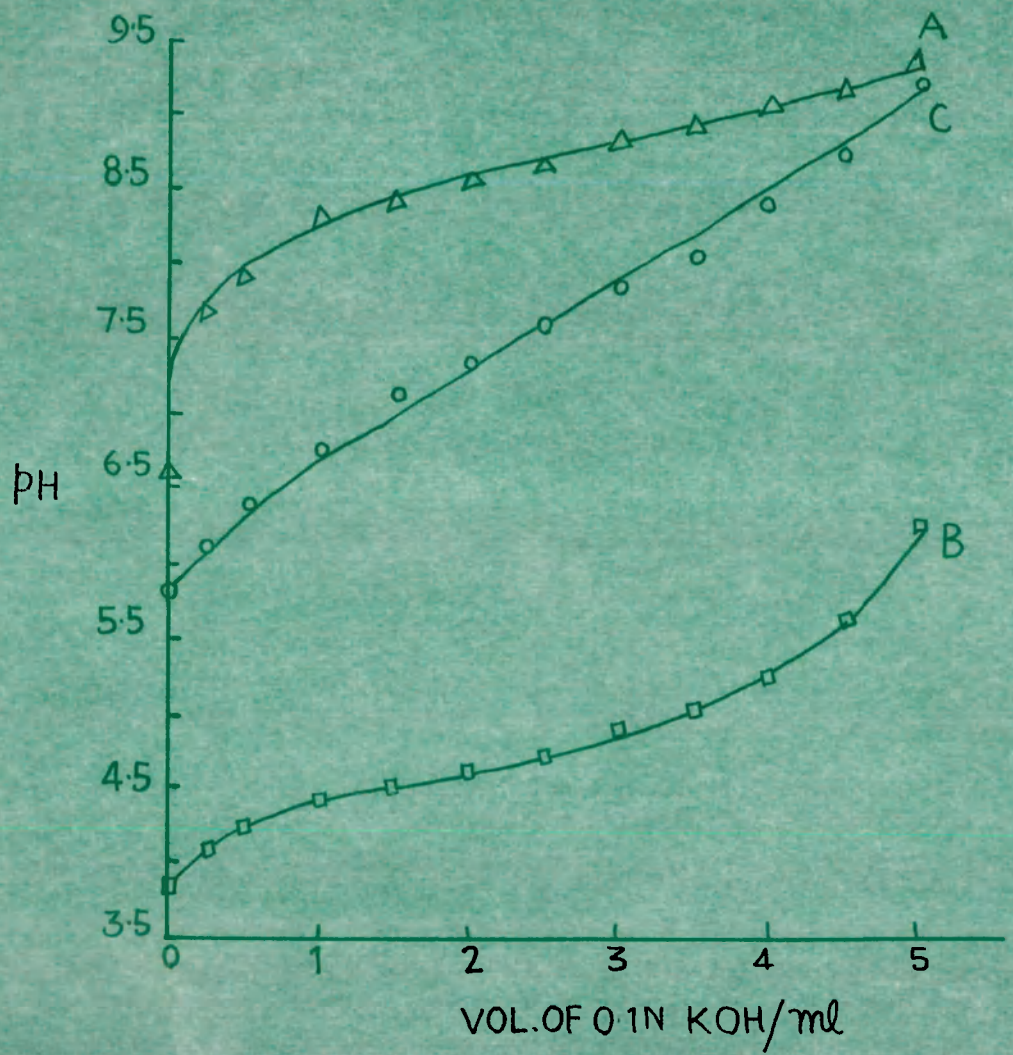
(B) = 50 ml of 0.005M Vanadyl Sulphate (in the cell)

(C) = 25 ml of 0.02M L-Proline + 25 ml of 0.01M Vanadyl Sulphate (in the cell)

(Vide Fig. No.25 B)

FIGURE NO. 26B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-LEUCINE (IN THE CELL)

B = 50 ml OF 0·005M $VOSO_4$ (IN THE CELL)

C = 25 ml OF 0·02M L-LEUCINE + 25 ml OF 0·01M $VOSO_4$ (IN THE CELL)

VIDE TABLE NO. 26B

T A B L E No.26 B

pH-metric titrations of VO^{2+}-L-Leucine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.60	3.85	5.80
0.25	7.70	4.10	6.10
0.50	7.90	4.25	6.40
1.00	8.30	4.40	6.75
1.50	8.40	4.50	7.10
2.00	8.55	4.60	7.30
2.50	8.65	4.75	7.60
3.00	8.80	4.90	7.85
3.50	8.90	5.00	8.05
4.00	9.05	5.25	8.40
4.50	9.15	5.60	8.75
5.00	9.30	6.25	9.25

(A) = 50 ml of 0.01M L-Leucine (in the cell)

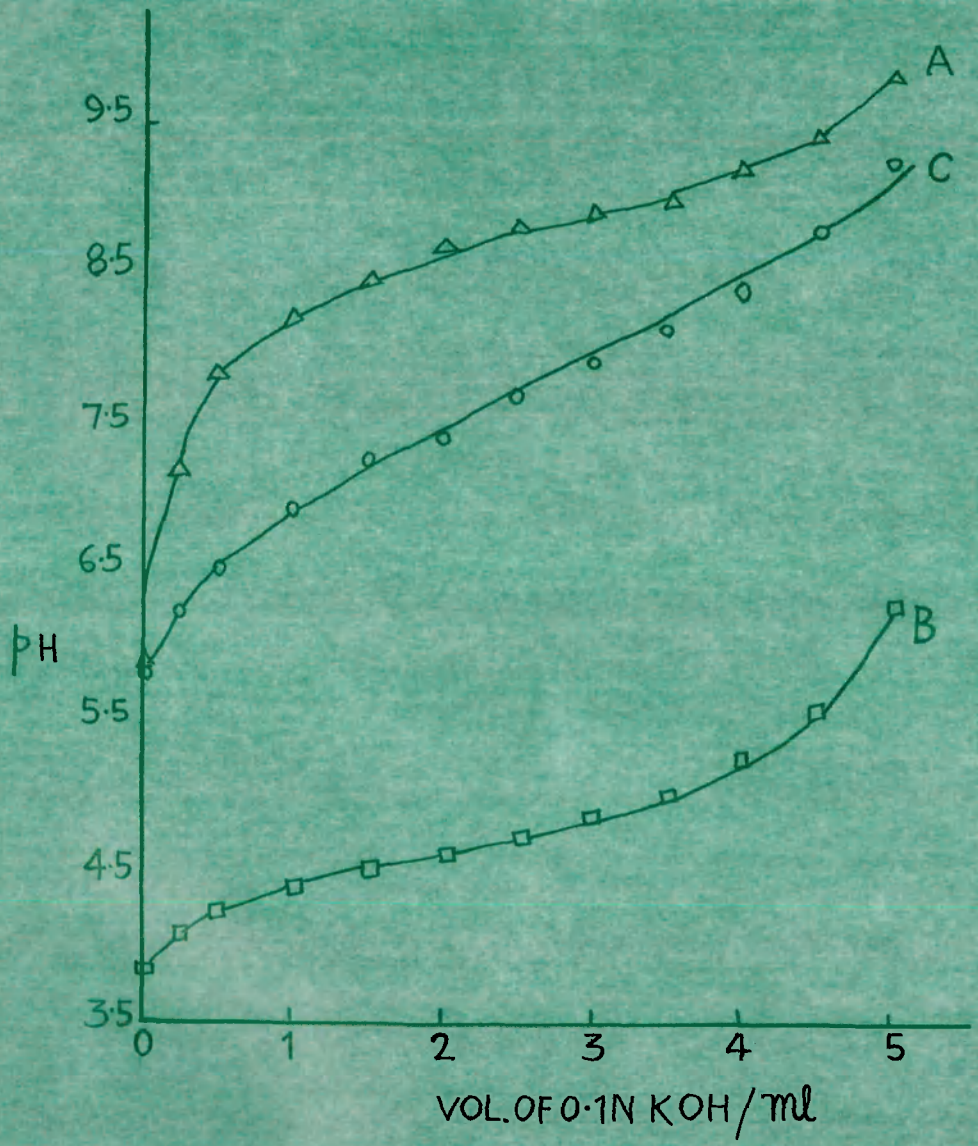
(B) = 50 ml of 0.005M Vanadyl Sulphate (in the cell)

(C) = 25 ml of 0.02M L-Leucine + 25 ml of 0.01M Vanadyl Sulphate (in the cell)

(Vide Fig. No.26 B)

FIGURE NO.27B

PH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL-α-ALANINE (IN THE CELL)

B = 50 ml OF 0·005M $VOSO_4$ (IN THE CELL)

C = 25 ml OF 0·02M DL-α-ALANINE + 25 ml OF 0·01M $VOSO_4$ (IN THE CELL)

VIDE TABLE NO.27B

T A B L E No.27 B

pH-metric titrations of VO^{2+}-DL-∝-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	3.85	5.85
0.25	7.20	4.10	6.25
0.50	7.85	4.25	6.55
1.00	8.20	4.40	6.90
1.50	8.50	4.50	7.25
2.00	8.70	4.60	7.45
2.50	8.80	4.75	7.70
3.00	8.90	4.90	7.90
3.50	9.00	5.00	8.10
4.00	9.20	5.25	8.45
4.50	9.40	5.60	8.80
5.00	9.80	6.25	9.25

(A) = 50 ml of 0.01M DL-∝-Alanine (in the cell)

(B) = 50 ml of 0.005M Vanadyl Sulphate (in the cell)

(C) = 25 ml of 0.02M DL-∝-Alanine + 25 ml of 0.01M Vanadul Sulphate (in the cell)

(Vide Fig. No.27 B)

T A B L E No.21 C

pH-metric titration of L-Asparagine (0.01M ; pK_a = 8.85) and Vanadyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.70	xx	xx	xx	xx
0.25	6.00	0.10	-4.8722	3.9156	xx
0.50	6.40	0.20	-4.4958	3.9883	xx
1.00	6.75	0.40	-4.1945	4.0042	xx
1.50	7.10	0.57	-3.8995	4.0443	xx
2.00	7.35	0.74	-3.7108	xx	xx
2.50	7.60	0.93	-3.5308	xx	xx
3.00	7.80	1.11	-3.4115	xx	xx
3.50	8.10	1.26	-3.2112	xx	3.0177
4.00	8.40	1.42	-3.1365	xx	3.0045
4.50	8.80	1.56	-3.8085	xx	2.9154
5.00	9.20	1.81	-2.5910	xx	xx

Mean log K' = 3.98

Mean log K" = 2.97

$\log K_s$ = 3.98 + 2.97 = 6.95 Calculated

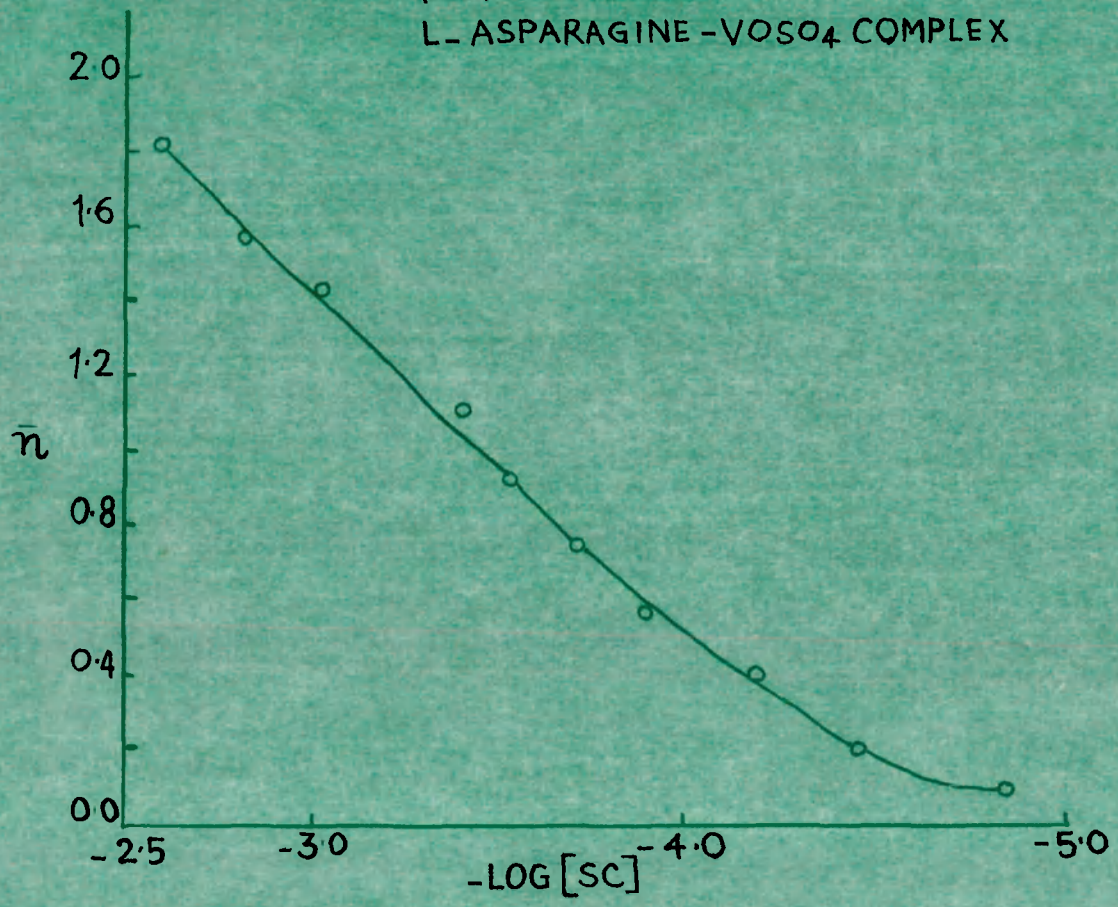
$\log K_s$ = 6.90 Graphically.

(Vide Fig. No.21 C)

FIGURE NO. 21C

FORMATION CURVE

L-ASPARAGINE-$VOSO_4$ COMPLEX

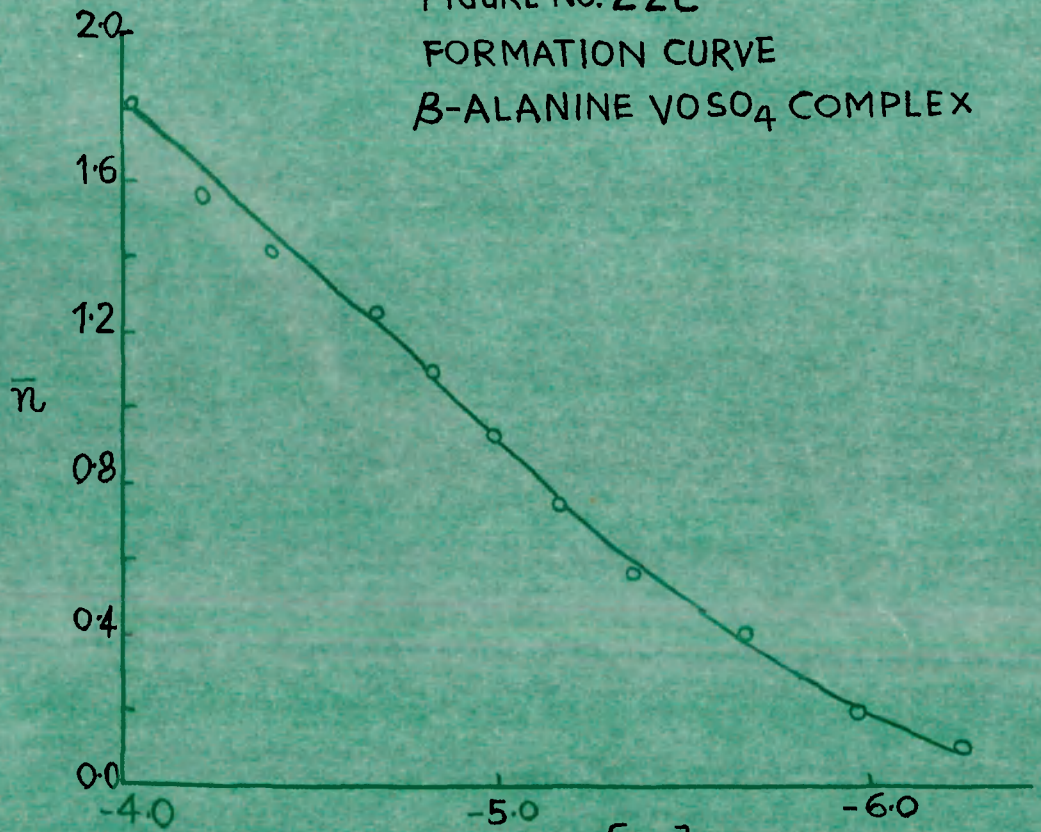


VIDE TABLE NO. 21C

FIGURE NO. 22C

FORMATION CURVE

β-ALANINE $VOSO_4$ COMPLEX



VIDE TABLE NO. 22C

T A B L E No.22 C

pH-metric titration of β-Alanine (0.01M ; pK_a = 9.87) and Vanadyl Sulphate(0.005M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.15	0.10	-6.2322	5.2756	xx
0.50	6.45	0.20	-5.9558	5.3483	xx
1.00	6.80	0.40	-5.6545	5.4642	xx
1.50	7.15	0.57	-5.3595	5.5043	xx
2.00	7.40	0.74	-5.1708	xx	xx
2.50	7.65	0.93	-4.9905	xx	xx
3.00	7.90	1.11	-4.8215	xx	xx
3.50	8.15	1.26	-4.6712	xx	4.4777
4.00	8.45	1.42	-4.3965	xx	4.3656
4.50	8.90	1.56	-4.2185	xx	4.3254
5.00	9.35	1.81	-4.0510	xx	xx

Mean log K' = 5.39

Mean log K" = 4.38

$\log K_a$ = 5.39 + 4.38 = 9.77 Calculated

$\log K_a$ = 9.80 Graphically.

(Vide Fig. No.22 C)

T A B L E No.23 C

pH-metric titration of DL-Serine (0.01M ; pK_s = 9.15) and Vanadyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.75	xx	xx	xx	xx
0.25	5.95	0.10	-5.2222	4.2656	xx
0.50	6.35	0.20	-4.8458	4.2883	xx
1.00	6.70	0.40	-4.5445	4.3342	xx
1.50	7.05	0.57	-4.2495	4.3943	xx
2.00	7.30	0.74	-4.0608	xx	xx
2.50	7.50	0.93	-3.9308	xx	xx
3.00	7.70	1.11	-3.5115	xx	xx
3.50	8.10	1.26	-3.4112	xx	3.2177
4.00	8.50	1.42	-3.2365	xx	3.2245
4.50	8.75	1.56	-3.1585	xx	3.2654
5.00	9.15	1.81	-3.0410	xx	xx

Mean log K' = 4.31

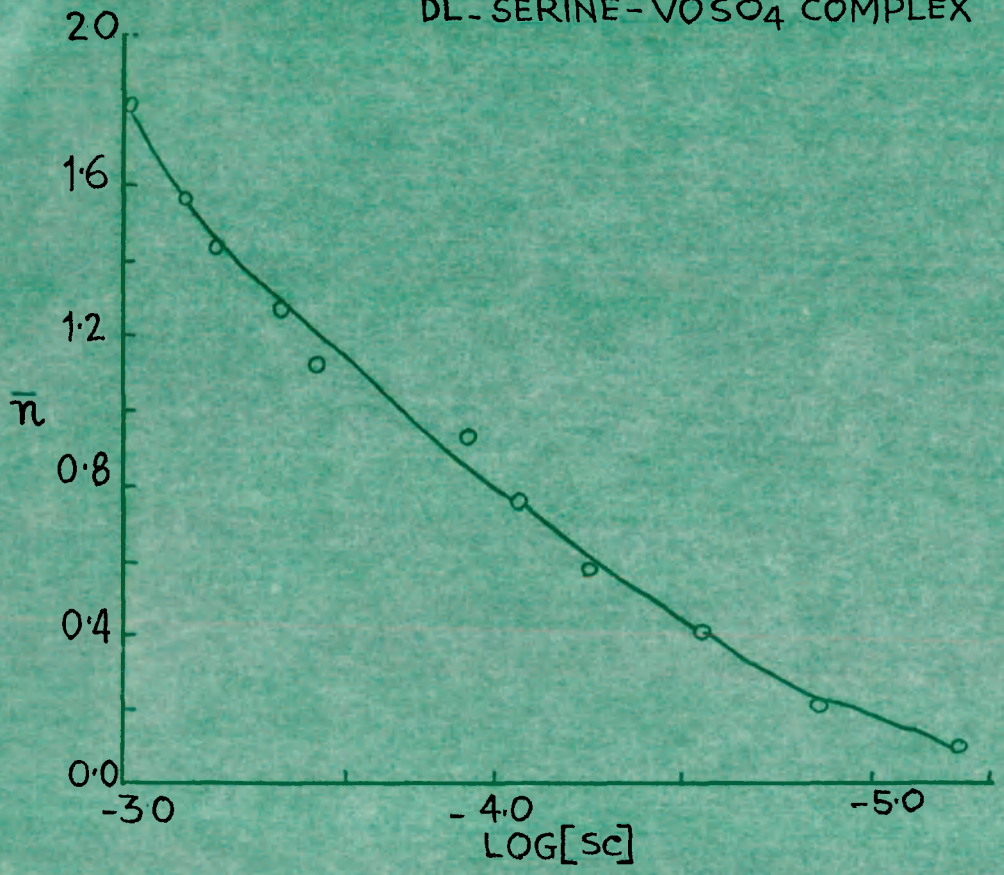
Mean log K" = 3.23

$\log K_s$ = 4.31 + 3.23 = 7.54 Calculated

$\log K_s$ = 7.50 Graphically.

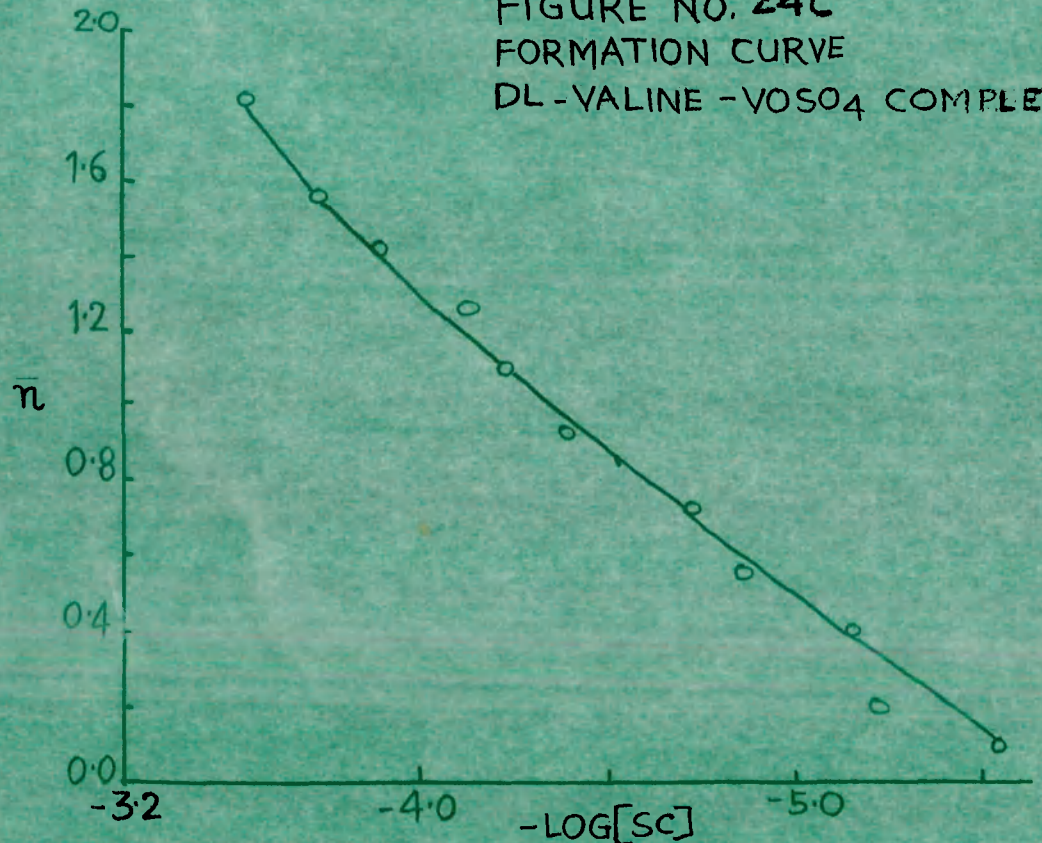
(Vide Fig. No.23 C)

FIGURE NO. 23C
FORMATION CURVE
DL-SERINE-$VOSO_4$ COMPLEX



VIDE TABLE NO. 23C

FIGURE NO. 24C
FORMATION CURVE
DL-VALINE-$VOSO_4$ COMPLEX



VIDE TABLE NO. 24C

T A B L E No.24 C

pH-metric titration of DL-Valine (0.01M ; pK_a = 9.71) and Vanadyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.75	xx	xx	xx	xx
0.25	6.20	0.10	-5.5322	4.5756	xx
0.50	6.55	0.20	-5.2058	4.5983	xx
1.00	6.65	0.40	-5.1545	4.9642	xx
1.50	7.00	0.57	-4.8595	5.0043	xx
2.00	7.30	0.74	-4.7207	xx	xx
2.50	7.60	0.93	-4.3908	xx	xx
3.00	7.85	1.11	-4.2215	xx	xx
3.50	8.05	1.26	-4.1212	xx	3.9237
4.00	8.40	1.42	-3.8965	xx	3.8645
4.50	8.75	1.56	-3.7185	xx	3.8254
5.00	9.50	1.81	-3.3510	xx	xx

Mean log K' = 4.78

Mean log K" = 3.87

$\log K_g$ = 4.78 + 3.87 = 8.65 Calculated

$\log K_g$ = 8.65 Graphically.

(Vide Fig. No.24 C)

T A B L E No.25 C

pH-metric titration of L-Proline (0.01M ; pK_a = 10.60) and Vanadyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.05	0.10	-6.5722	5.6156	xx
0.50	6.40	0.20	-6.2458	5.6386	xx
1.00	6.75	0.40	-5.9445	5.7542	xx
1.50	7.10	0.57	-5.6495	5.7943	xx
2.00	7.45	0.74	-5.3608	xx	xx
2.50	7.65	0.93	-5.2308	xx	xx
3.00	7.95	1.11	-5.0118	xx	xx
3.50	8.25	1.26	-4.8112	xx	4.6177
4.00	8.50	1.42	-4.6865	xx	4.6545
4.50	8.85	1.56	-4.5085	xx	4.6654
5.00	9.25	1.81	-4.3910	xx	xx

Mean log K' = 5.69

Mean log K" = 4.64

$\log K_s$ = 5.69 + 4.64 = 10.33 Calculated

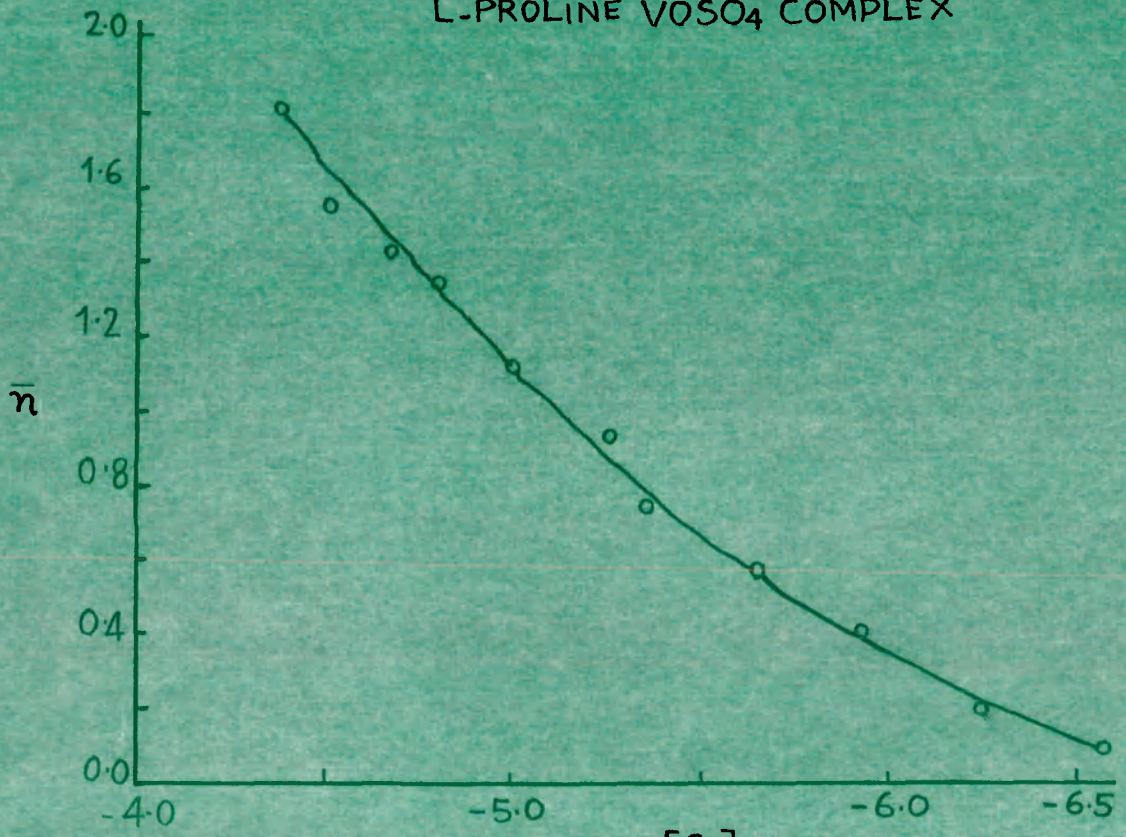
$\log K_s$ = 10.30 Graphically.

(Vide Fig. No.25 C)

FIGURE NO. 25C

FORMATION CURVE

L-PROLINE $VOSO_4$ COMPLEX

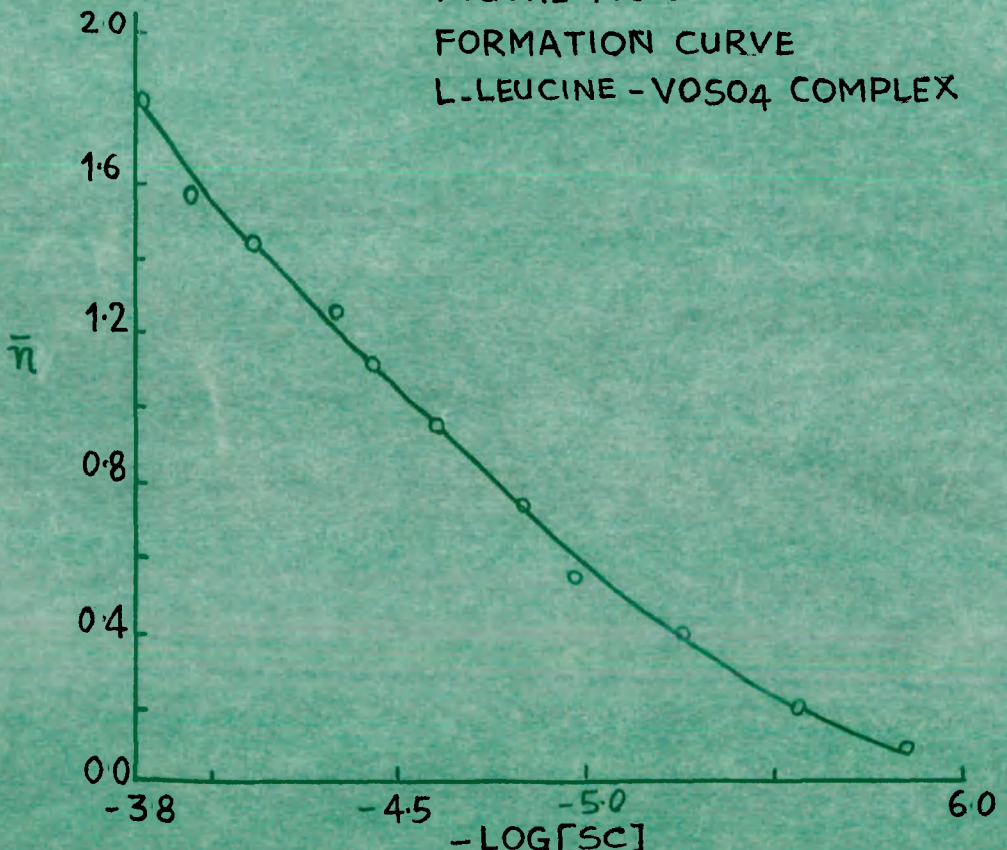


VIDE TABLE NO. 25C

FIGURE NO. 26C

FORMATION CURVE

L-LEUCINE - $VOSO_4$ COMPLEX



VIDE TABLE NO. 26C

TABLE No.26 C

pH-metric titration of L-Leucine (0.01M ; pK_a = 9.92) and Vanadyl Sulphate (0.005M), all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.10	0.10	-5.8422	4.8856	xx
0.50	6.40	0.20	-5.5658	4.9584	xx
1.00	6.75	0.40	-5.2645	5.0742	xx
1.50	7.10	0.57	-4.9695	5.1143	xx
2.00	7.30	0.74	-4.8308	xx	xx
2.50	7.60	0.93	-4.6008	xx	xx
3.00	7.85	1.11	-4.4315	xx	xx
3.50	8.05	1.26	-4.3312	xx	4.1380
4.00	8.40	1.42	-4.1065	xx	4.0745
4.50	8.75	1.56	-3.9385	xx	4.0454
5.00	9.25	1.81	-3.8210	xx	xx

Mean log K' = 5.00

Mean log K" = 4.08

$\log K_s$ = 5.00 + 4.08 = 9.08 Calculated

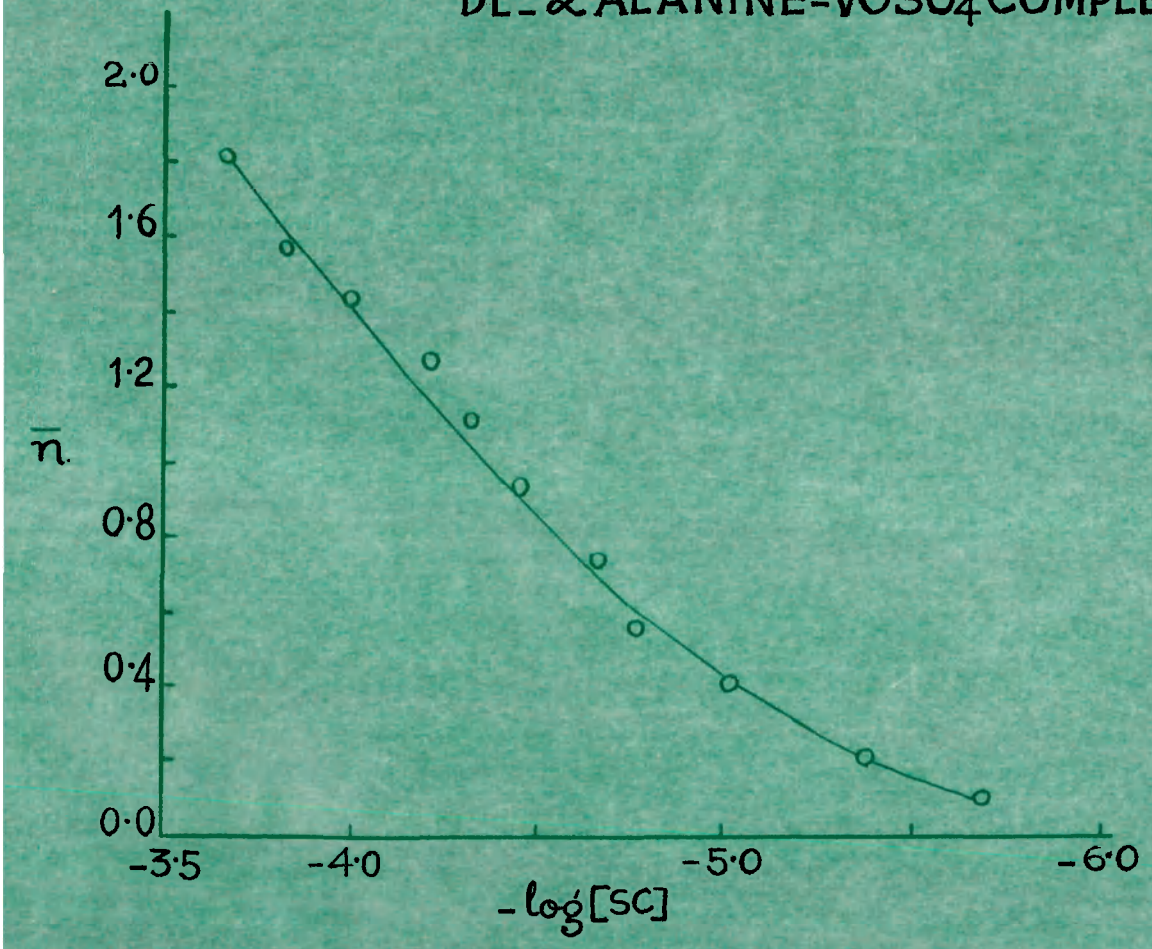
$\log K_s$ = 9.10 Graphically.

(Vide Fig. No.26 C)

FIGURE No.27c

FORMATION CURVE

DL-∝ ALANINE-$VOSO_4$ COMPLEX



VIDE TABLE No.27c

T A B L E No.27 C

pH-metric titration of DL-α-Alanine (0.01M ; pK_a = 9.86) and Vanadyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.25	0.10	-5.6322	4.6756	xx
0.50	6.55	0.20	-5.3558	4.7483	xx
1.00	6.90	0.40	-5.0545	4.7652	xx
1.50	7.25	0.57	-4.7595	4.8043	xx
2.00	7.45	0.74	-4.6608	xx	xx
2.50	7.70	0.93	-4.4408	xx	xx
3.00	7.90	1.11	-4.3224	xx	xx
3.50	8.10	1.26	-4.2212	xx	4.1739
4.00	8.45	1.42	-3.9965	xx	3.9685
4.50	8.80	1.56	-3.8185	xx	3.9289
5.00	9.25	1.81	-3.6756	xx	xx

Mean log K' = 4.74

Mean log K" = 4.01

$\log K_s$ = 4.74 + 4.01 = 8.75 Calculated

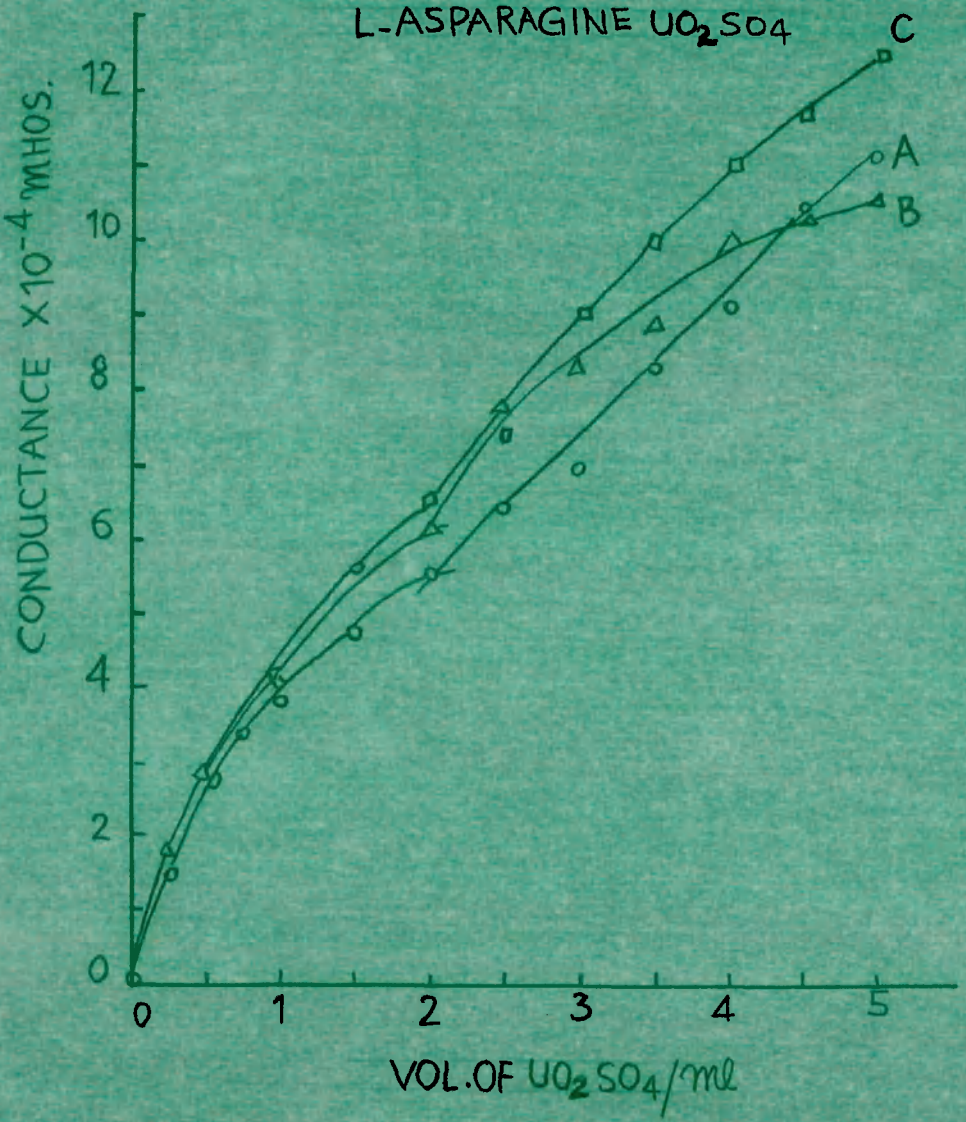
$\log K_s$ = 8.75 Graphically.

(Vide Fig. No.27 C)

FIGURE NO. 28A

REVERSE CONDUCTOMETRIC TITRATIONS

L-ASPARAGINE UO_2SO_4



A= 40 ml OF 0·005 M L-ASPARAGINE Vs. 0·1M UO_2SO_4

B= 40 ml OF 0·0045 ML-ASPARAGINE Vs. 0·099 M UO_2SO_4

C= 40 ml OF 0·0041 M L-ASPARAGINE Vs. 0·083 M UO_2SO_4

VIDE TABLE NO. 28A

T A B L E No.28 A

Conductometric-titrations (Reverse)

L-Asparagine-Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.158	0.166	0.172
0.5	2.94	2.76	2.85
1.0	3.84	4.00	4.16
1.5	4.76	5.25	5.25
2.0	5.55	6.05	6.25
2.5	6.25	7.70	7.45
3.0	6.90	8.35	9.09
3.5	8.35	8.70	10.00
4.0	9.09	10.00	11.09
4.5	10.50	10.40	11.75
5.0	11.09	10.50	12.50

1st.titration :- 40 ml of 0.005M L-Asparagine Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0045M L-Asparagine Vs. 0.099M Uranyl Sulphate

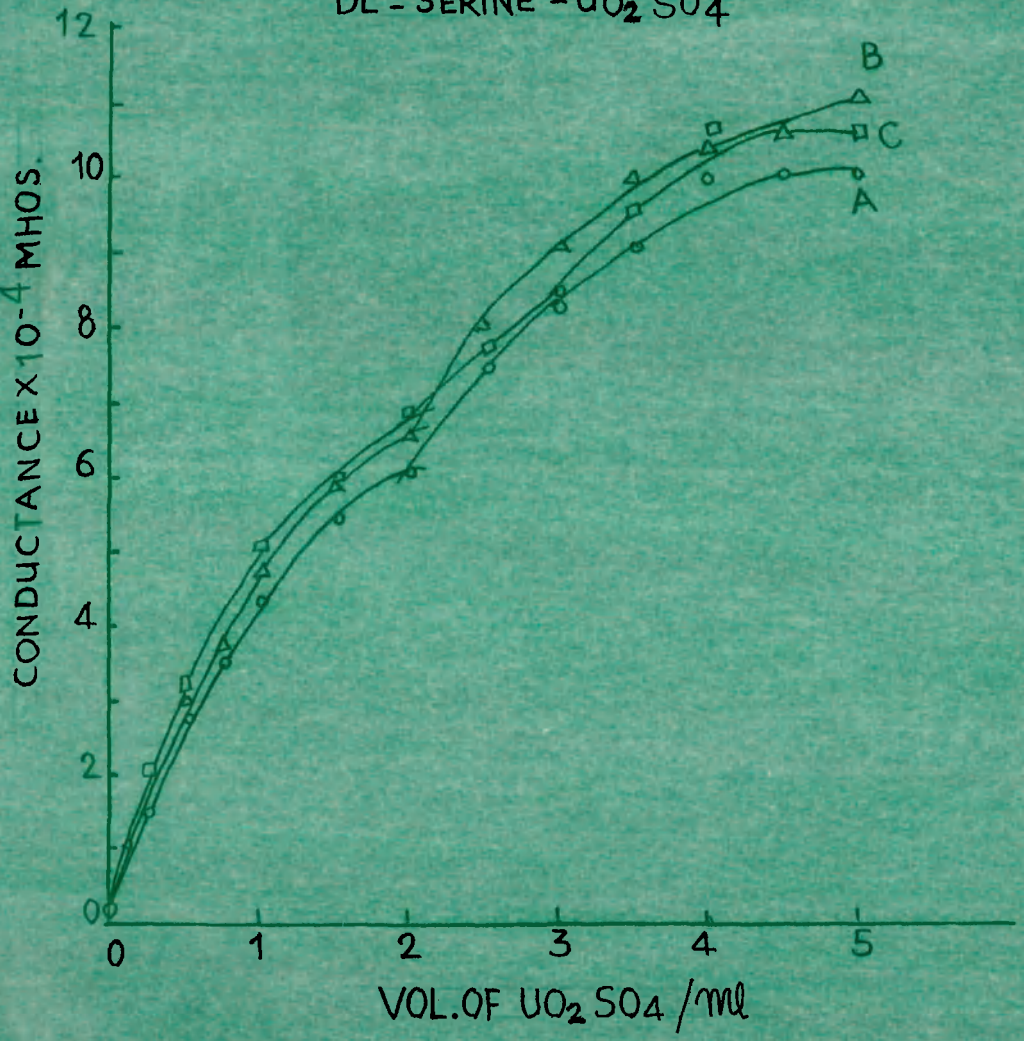
3rd.titration :- 40 ml of 0.0041M L-Asparagine Vs. 0.083M Uranyl Sulphate

(Vide Fig. No. 28 A)

FIGURE NO. 29A

REVERSE CONDUCTOMETRIC TITRATIONS.

DL - SERINE - UO_2SO_4



A = 40 ml OF 0·005 M DL - SERINE Vs. 0·1 M UO_2SO_4

B = 40 ml OF 0·0045 M DL - SERINE Vs. 0·099 M UO_2SO_4

C = 40 ml OF 0·0041 M DL - SERINE Vs. 0·083 M UO_2SO_4

VIDE TABLE NO. 29A

TABLE No.29 A

Conductometric - titrations (Reverse)

DL-Serine - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.20	0.28	0.21
0.5	2.77	2.85	3.12
1.0	4.34	4.76	5.00
1.5	5.42	5.71	5.88
2.0	6.00	6.25	6.66
2.5	7.70	8.00	7.45
3.0	8.33	9.09	8.33
3.5	9.09	10.0	9.52
4.0	10.00	10.50	10.50
4.5	10.00	10.50	10.50
5.0	10.00	11.1	10.50

1st.titration :- 40 ml of 0.005M DL- Serine
Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0045M DL-Serine
Vs. 0.099M Uranyl Sulphate

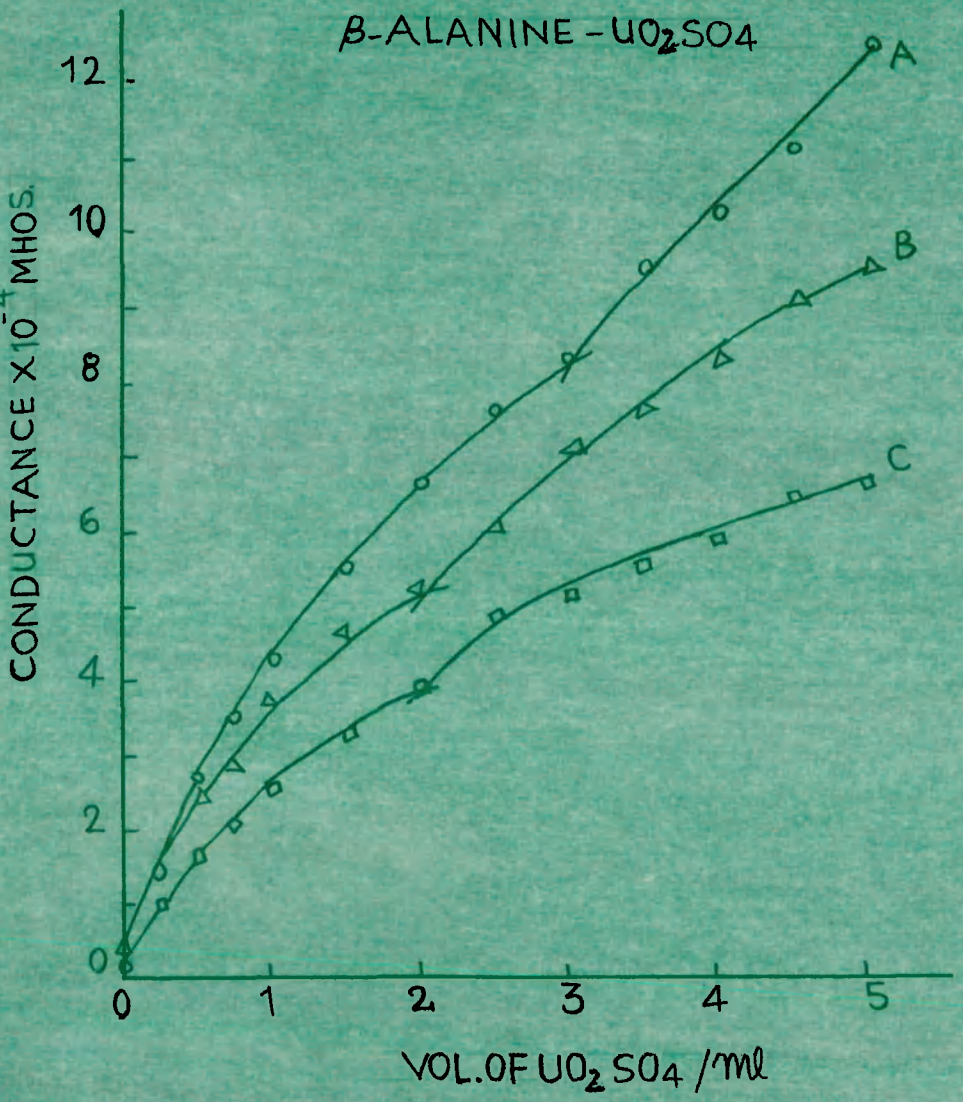
3rd.titration :- 40 ml of 0.0041M DL-Serine
Vs. 0.083M Uranyl Sulphate

(Vide Fig. No.29 A)

FIGURE NO. 30A

REVERSE CONDUCTOMETRIC TITRATIONS

β-ALANINE – UO_2SO_4



A = 60 ml OF 0·005 M β-ALANINE Vs. 0·1 M UO_2SO_4

B = 40 ml OF 0·0033 M β-ALANINE Vs. 0·066 M UO_2SO_4

C = 40 ml OF 0·002 M β-ALANINE Vs. 0·04 M. UO_2SO_4

VIDE TABLE NO. 30A

T A B L E No.30 A

Conductometric - titrations (Reverse)

β-Alanine - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.143	0.28	0.25
0.5	2.63	2.50	1.58
1.0	4.35	3.70	2.53
1.5	5.55	4.65	3.33
2.0	6.66	5.26	3.92
2.5	7.66	6.06	4.89
3.0	8.34	7.14	5.13
3.5	9.25	7.66	5.25
4.0	10.20	8.34	5.86
4.5	11.10	9.07	6.25
5.0	12.50	9.52	6.66

1st.titration :- 60 ml of 0.005M β-Alanine Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0033M β-Alanine Vs. 0.066M Uranyl Sulphate

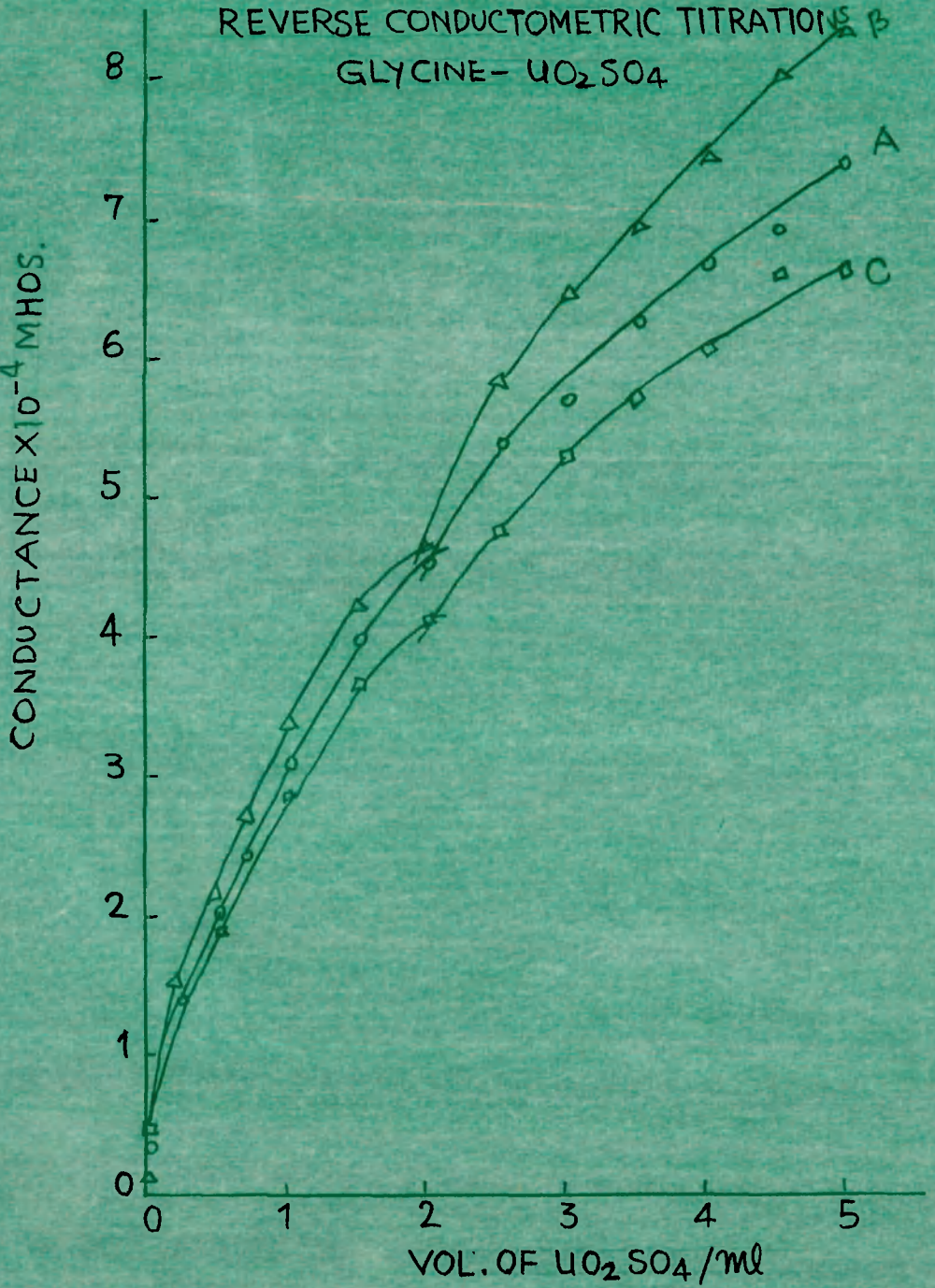
3rd.titration :- 40 ml of 0.002M β-Alanine Vs. 0.04M Uranyl Sulphate

(Vide Fig. No.30 A)

FIGURE NO. 31A

REVERSE CONDUCTOMETRIC TITRATIONS

GLYCINE – UO_2SO_4



A = 40 ml OF 0·005 M GLYCINE Vs. 0·1 M UO_2SO_4

B = 40 ml OF 0·0033 M GLYCINE Vs. 0·066 M UO_2SO_4

C = 20 ml OF 0·004 M GLYCINE Vs. 0·04 M UO_2SO_4

VIDE TABLE NO. 31A

T A B L E No. 31 A

Conductometric - titrations (Reverse)

Glycine - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.37	0.182	0.454
0.5	2.04	2.17	1.92
1.0	3.13	3.44	2.93
1.5	4.00	4.25	3.70
2.0	4.55	5.12	4.16
2.5	5.40	5.86	4.76
3.0	5.71	6.45	5.26
3.5	6.25	6.90	5.71
4.0	6.66	7.40	6.05
4.5	6.90	8.00	6.66
5.0	7.40	8.33	6.66

1st.titration :- 40 ml of 0.005M Glycine
Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0033M Glycine
Vs. 0.066M Uranyl Sulphate

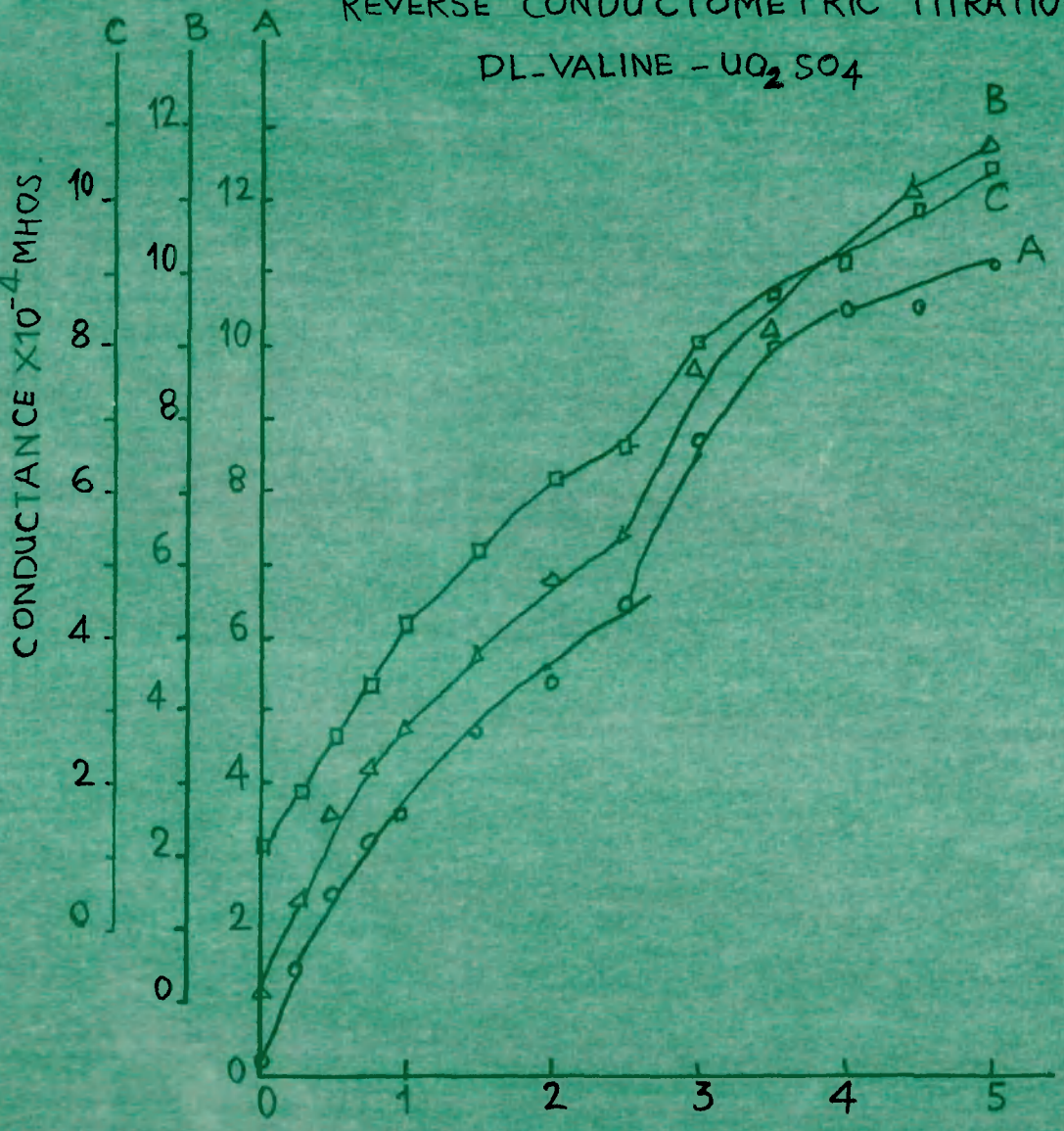
3rd.titration :- 20 ml of 0.004M Glycine
Vs. 0.04M Uranyl Sulphate

(Vide Fig. No.31 A)

FIGURE NO. 32A

REVERSE CONDUCTOMETRIC TITRATIONS.

DL-VALINE - UO_2SO_4



A = 50 ml OF 0·005 M DL-VALINE Vs. 0·1 M UO_2SO_4

B = 50 ml OF 0·0045 M DL-VALINE Vs. 0·099 M UO_2SO_4

C = 50 ml OF 0·0041 M DL-VALINE Vs. 0·088 M UO_2SO_4

VIDE TABLE NO. 32A

TABLE No.32 A

Conductometric - titrations (Reverse)

DL-Valine - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.18	0.19	0.196
0.5	2.50	2.63	2.70
1.0	3.64	3.82	4.25
1.5	4.76	4.76	5.26
2.0	5.42	5.88	6.25
2.5	6.25	6.45	6.66
3.0	8.70	8.70	8.00
3.5	10.00	9.09	8.70
4.0	10.50	11.10	9.09
4.5	10.50	11.10	10.00
5.0	11.10	11.75	10.50

1st.titration :- 50 ml of 0.005M DL-Valine
Vs. 0.1M Uranyl Sulphate

2nd.titration :- 50 ml of 0.0045M DL-Valine
Vs. 0.099M Uranyl Sulphate

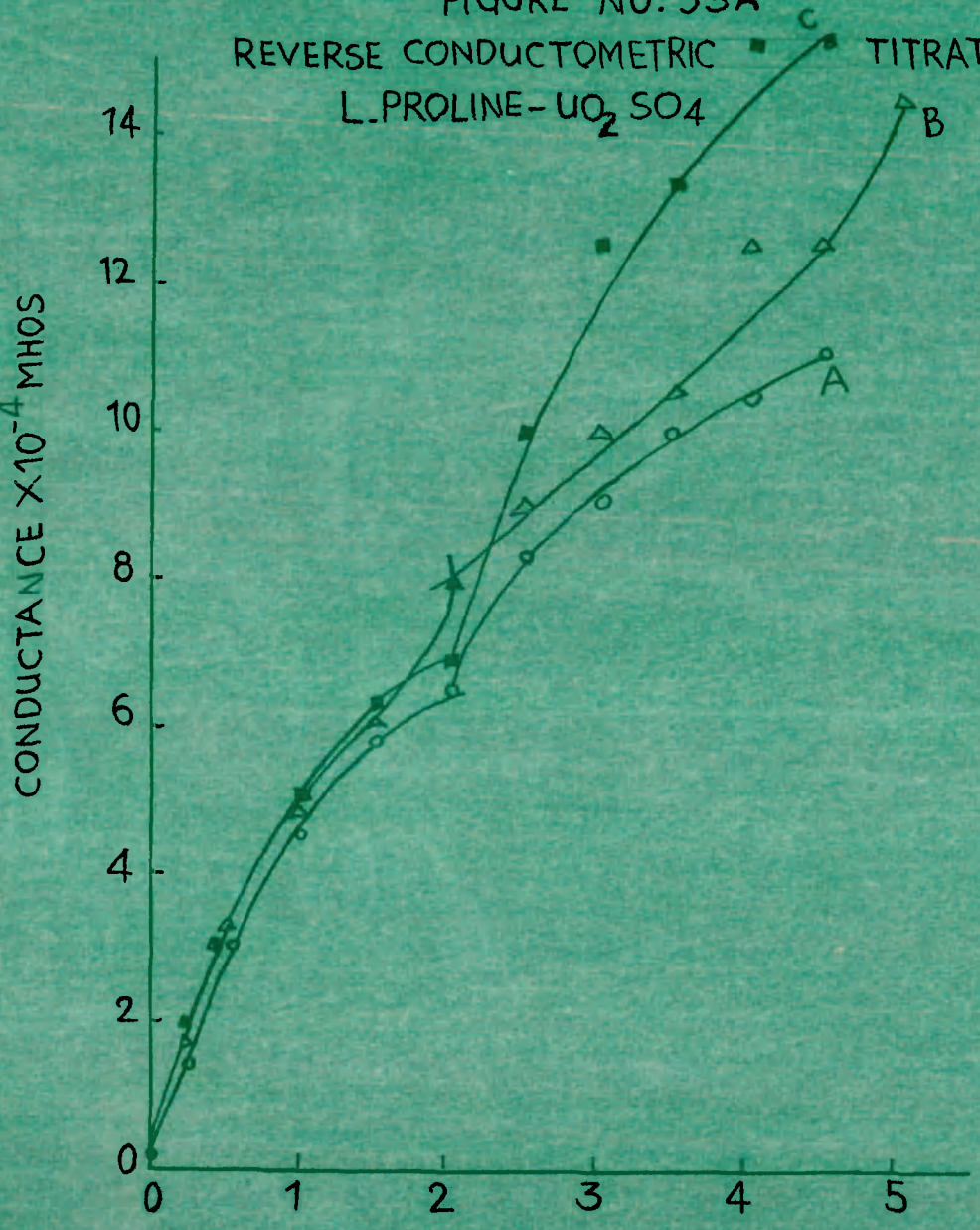
3rd.titration :- 50 ml of 0.0041M DL-Valine
Vs. 0.083M Uranyl Sulphate

(Vide Fig. No.32 A)

FIGURE NO. 33A

REVERSE CONDUCTOMETRIC TITRATIONS

L-PROLINE - UO_2SO_4



A = 40 ml OF 0·005 M L-PROLINE Vs. 0·1 M UO_2SO_4

B = 40 ml OF 0·0045 M L-PROLINE Vs. 0·099 M UO_2SO_4

C = 40 ml OF 0·0041 M L-PROLINE Vs. 0·083 M UO_2SO_4

VIDE TABLE NO. 33A

T A B L E No.33 A

Conductometric - titrations (Reverse)

L - Proline - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.161	0.164	0.166
0.5	3.03	3.23	3.33
1.0	4.55	4.76	5.00
1.5	5.87	6.06	6.25
2.0	6.25	8.00	6.90
2.5	8.33	0.09	10.00
3.0	9.09	10.00	12.50
3.5	10.00	10.50	13.31
4.0	10.50	12.50	15.54
4.5	10.50	12.50	15.54
5.0	11.09	14.25	16.65

1st.titration :- 40 ml of 0.005M L-Proline
Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0045M L-Proline
Vs. 0.099M Uranyl Sulphate

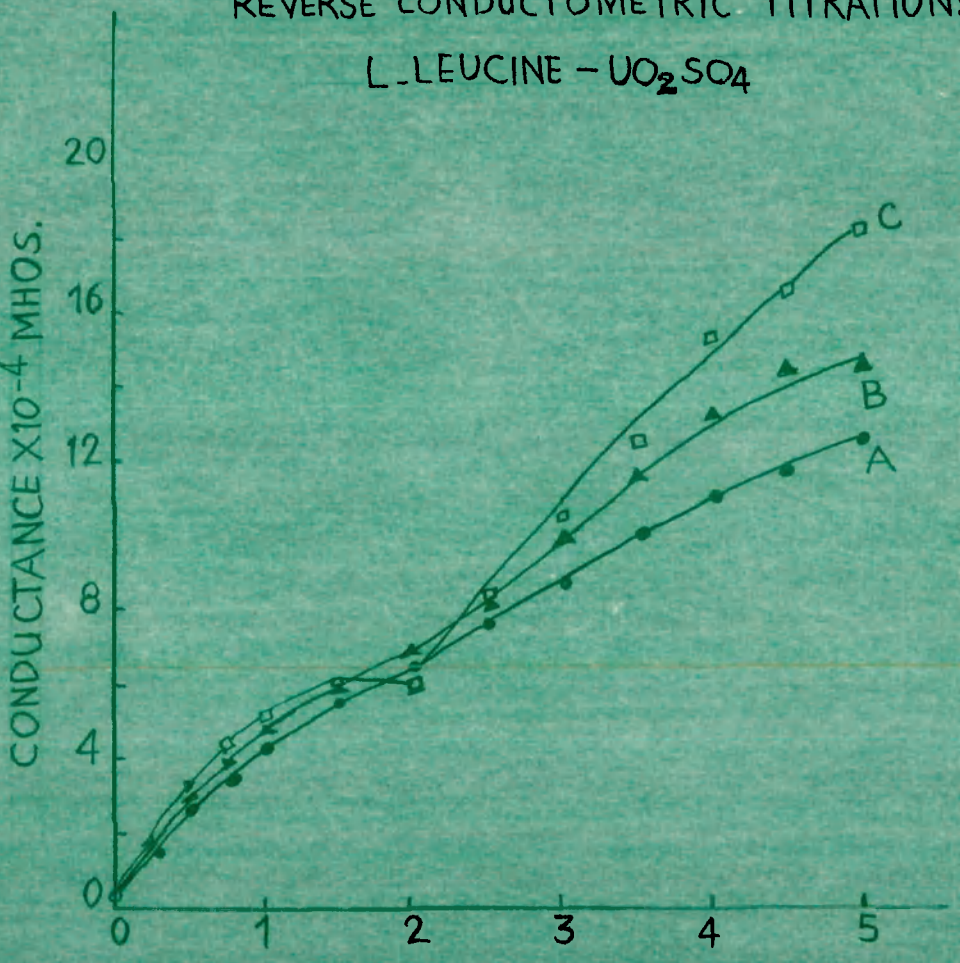
3rd.titration :- 40 ml of 0.0041M L-Proline
Vs. 0.083M Uranyl Sulphate

(Vide Fig. No.33 A)

FIGURE NO. 34A

REVERSE CONDUCTOMETRIC TITRATIONS.

L-LEUCINE – UO_2SO_4



A = 40 ml OF 0·005 M L-LEUCINE Vs. 0.1 M UO_2SO_4

B = 40 ml OF 0·045 M L-LEUCINE Vs. 0·099 UO_2SO_4

C = 40 ml OF 0·0041 M L-LEUCINE Vs. 0·08 M UO_2SO_4

VIDE TABLE NO. 34A

TABLE No.34 A

Conductometric - titrations (Reverse)

L-Leucine - Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.135	0.134	0.132
0.5	2.63	2.85	3.03
1.0	4.25	4.76	5.00
1.5	5.55	5.71	5.55
2.0	6.45	6.66	6.06
2.5	7.70	8.00	8.35
3.0	8.70	10.00	10.50
3.5	10.00	11.75	12.50
4.0	11.10	13.30	15.40
4.5	11.75	14.25	16.65
5.0	12.50	14.25	18.20

1st.titration :- 40 ml of 0.005M L-Leucine
Vs. 0.1M Uranyl Sulphate

2nd.titration :- 40 ml of 0.0045M L-Leucine
Vs. 0.099M Uranyl Sulphate

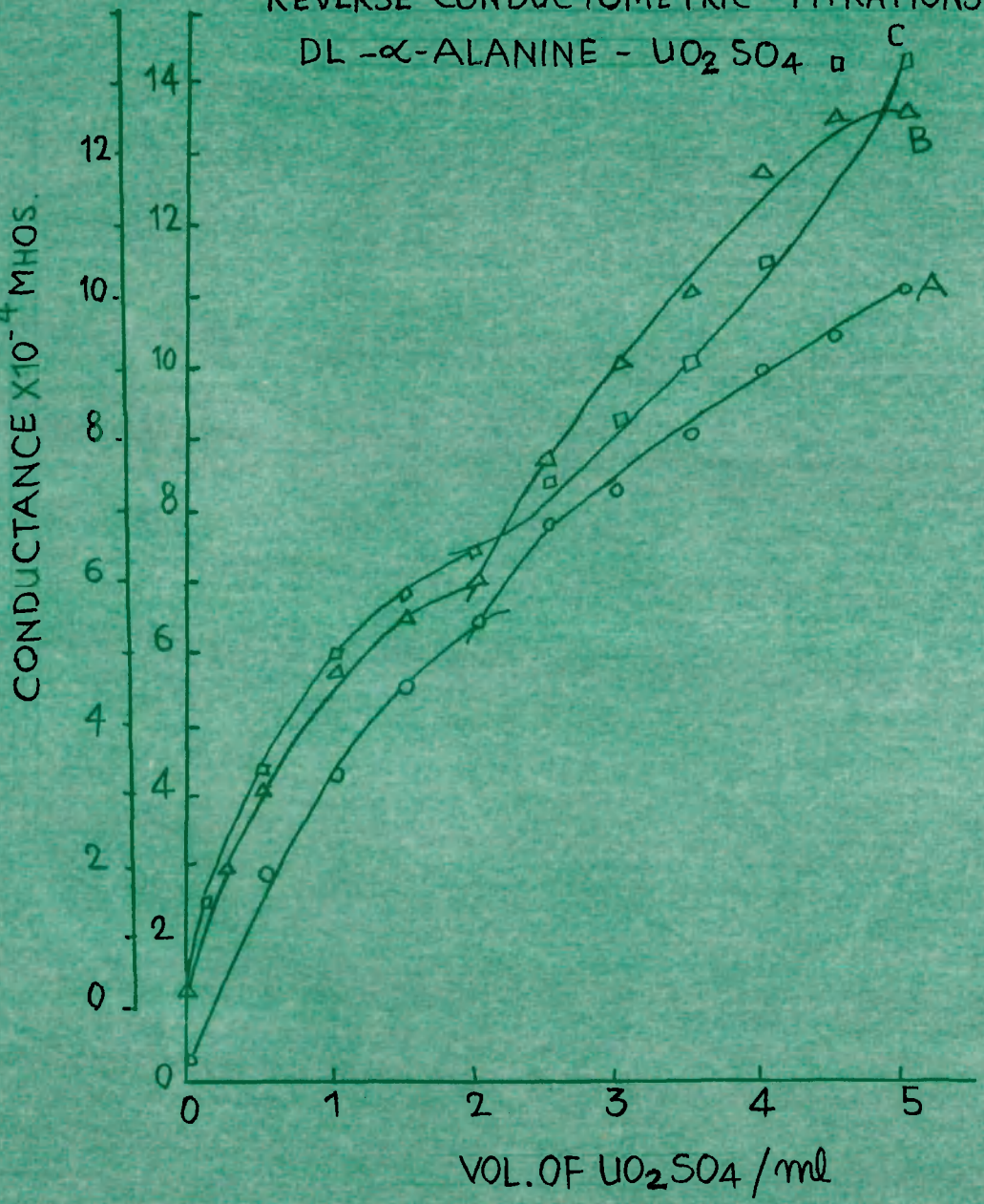
3rd.titration :- 40 ml of 0.0041M L-Leucine
Vs. 0.083M Uranyl Sulphate

(Vide Fig. No.34 A)

FIGURE NO. 35A

REVERSE CONDUCTOMETRIC TITRATIONS

DL -∝- ALANINE - UO_2SO_4



A = 40 ml OF 0·005 M DL - ∝ - ALANINE Vs. 0·1M UO_2SO_4

B = 40 ml OF 0·0045 M DL - ∝ - ALANINE Vs. 0·099M UO_2SO_4

C = 40 ml OF 0·0041 M DL - ∝ - ALANINE Vs. 0·083M UO_2SO_4

VIDE TABLE NO. 35A

TABLE No.35 A

Conductometric - titrations (Reverse)

DL- ∝- Alanine-Uranyl Sulphate Complex

Vol.of UO_2SO_4 added.(ml)	1st.titration. Conductance $x10^{-4}$mhos.	2nd.titration. Conductance $x10^{-4}$mhos.	3rd.titration. Conductance $x10^{-4}$mhos.
0.0	0.25	0.261	0.263
0.5	2.94	3.12	3.33
1.0	4.34	4.76	5.00
1.5	5.55	5.55	5.71
2.0	6.45	6.06	6.25
2.5	7.70	7.70	7.45
3.0	8.33	9.09	8.33
3.5	9.09	10.00	0.09
4.0	10.00	11.75	10.50
4.5	10.50	12.50	13.30
5.0	11.09	12.50	13.30

1st.titration :- 40 ml of 0.005M DL- ∝-Alanine Vs. 0.1 M Uranyl Sulphate

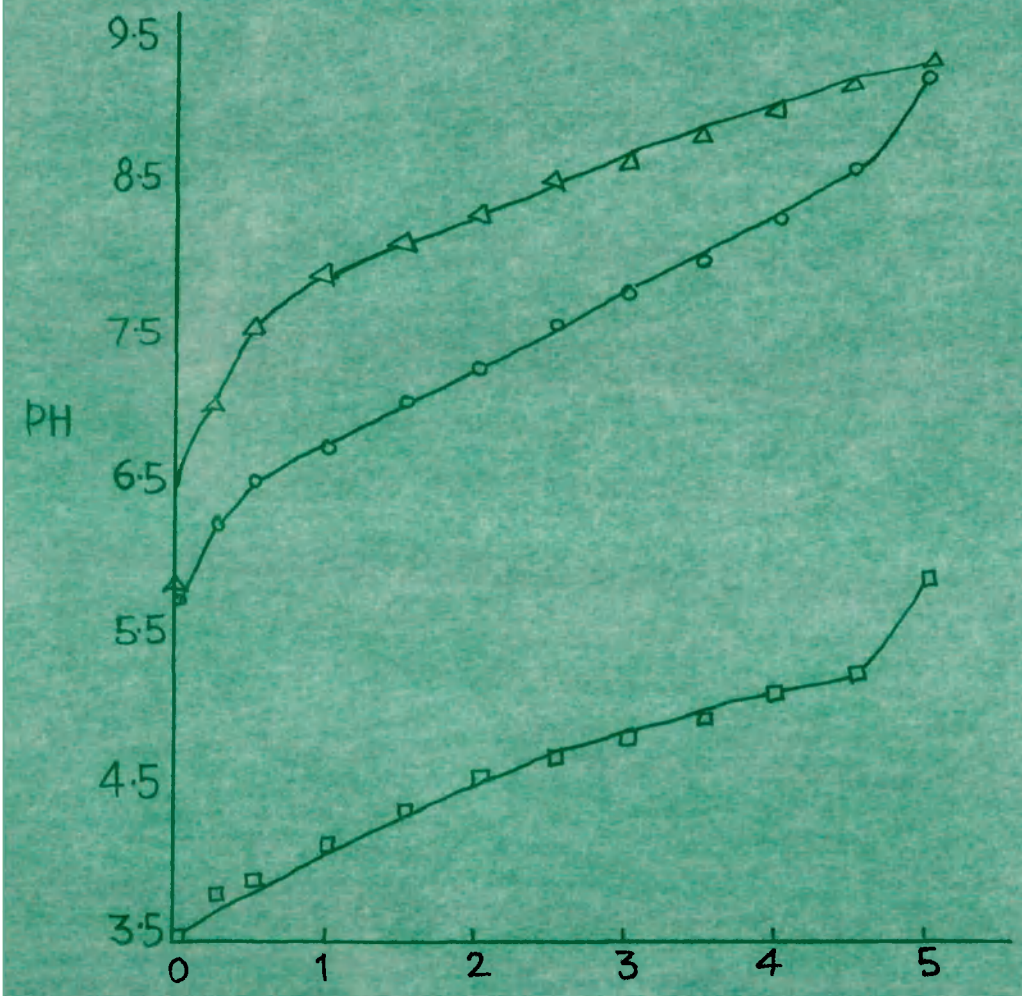
2nd.titration :- 40 ml of 0.0045M DL- ∝-Alanine Vs. 0.099M Uranyl Sulphate

3rd.titration :- 40 ml of 0.0041M DL- ∝-Alanine Vs. 0.083M Uranyl Sulphate

(Vide Fig. No.35 A)

FIGURE NO.28B

PH-METRIC TITRATIONS



A=50 ml OF 0·01M L-ASPARAGINE (IN THE CELL)

B = 50 ml OF 0·005 M URANYLSULPHATE (IN THE CELL)

C=25 ml OF 0·02ML-ASPARAGINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO.28B

T A B L E No.28 B

pH-metric titrations of UO_2^{2+}-L-Asparagine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	3.65	5.80
0.25	7.10	3.85	6.35
0.50	7.60	3.95	6.60
1.00	8.00	4.20	6.80
1.50	8.20	4.40	7.15
2.00	8.40	4.60	7.35
2.50	8.60	4.75	7.65
3.00	8.70	4.90	7.85
3.50	8.90	5.00	8.05
4.00	9.10	5.20	8.35
4.50	9.25	5.35	8.70
5.00	9.40	5.95	9.30

(A) = 50 ml of 0.01M L-Asparagine (in the cell)

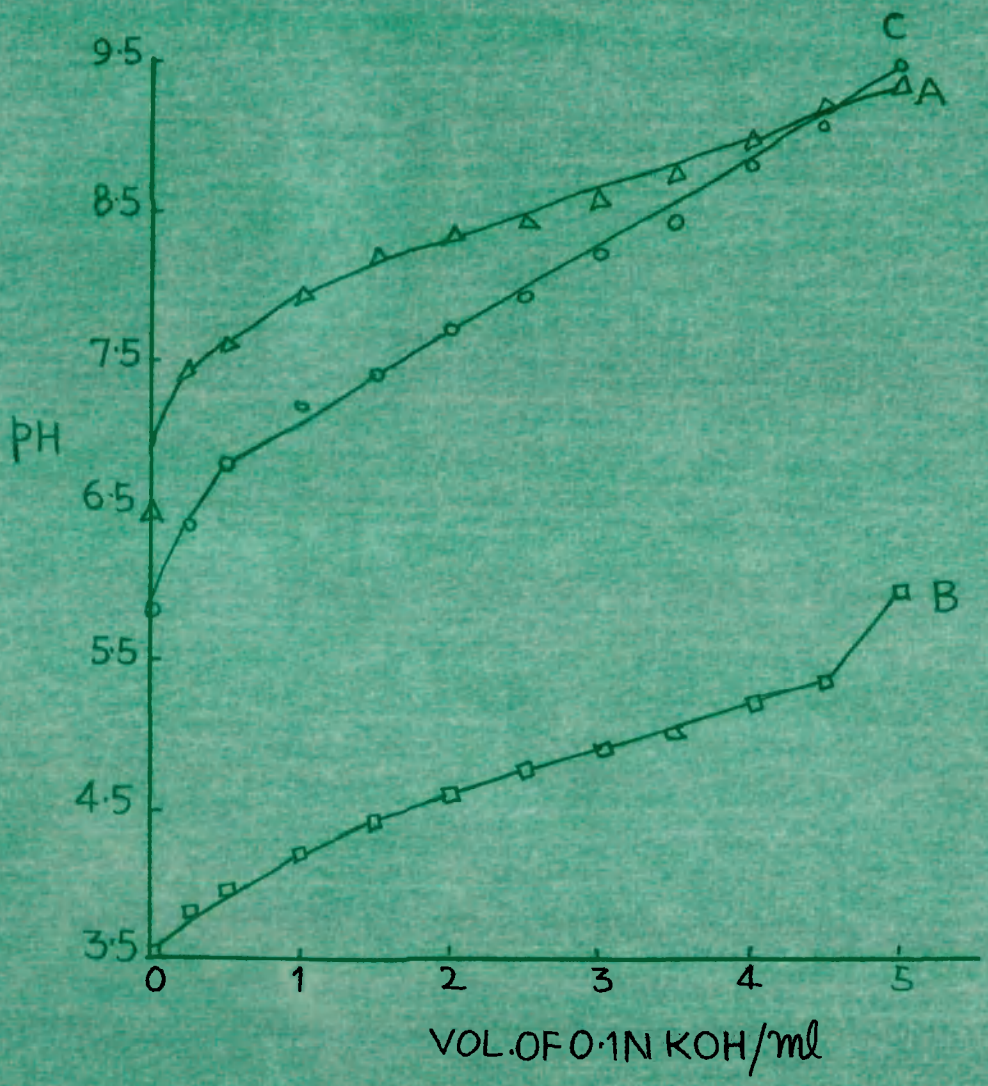
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M L-Asparagine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.28 B)

FIGURE NO. 29 B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL - SERINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02 M DL - SERINE + 25 ml OF 0·01 M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 29 B

T A B L E No.29 B

pH-metric titrations of UO_2^{2+}-DL-Serine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.65	5.85
0.25	7.40	3.85	6.40
0.50	7.60	3.95	6.80
1.00	7.90	4.20	7.20
1.50	8.20	4.40	7.40
2.00	8.30	4.60	7.70
2.50	8.40	4.75	7.90
3.00	8.50	4.90	8.20
3.50	8.70	5.00	8.40
4.00	8.95	5.20	8.80
4.50	9.20	5.35	9.05
5.00	9.35	5.95	9.40

(A) = 50 ml of 0.01M DL-Serine (in the cell)

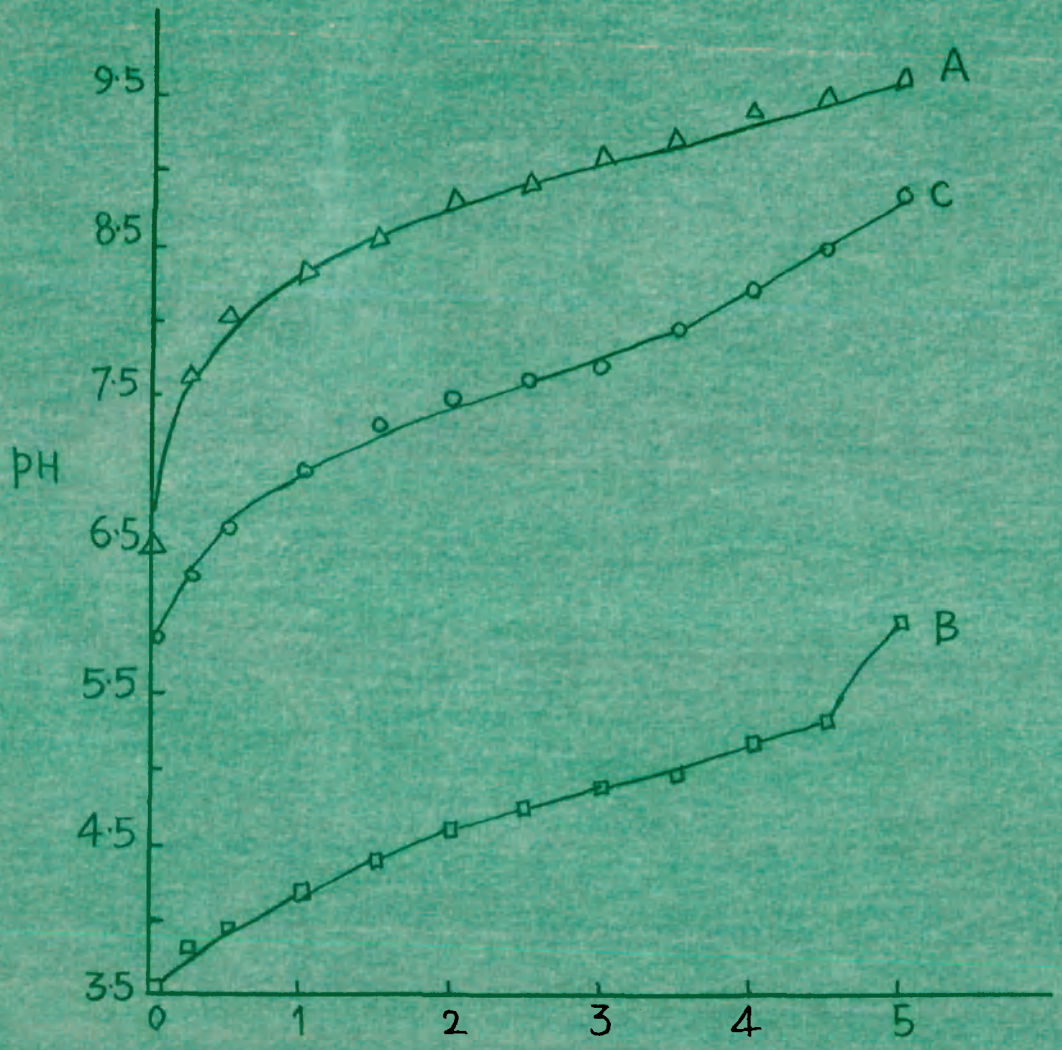
(B) = 50 ml of 0.005M Uranyl Sulphate (in the cell)

(C) = 25 ml of 0.02M DL-Serine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.29 B)

FIGURE NO. 30 B

PH-METRIC TITRATIONS



A=50 ml OF 0·01M β-ALANINE (IN THE CELL)

B=50 ml OF 0·005 M UO_2SO_4 (IN THE CELL)

C=25 ml OF 0·02 M β-ALANINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 30 B

T A B L E No.30 B

pH-metric titrations of UO_2^{2+}- β-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.65	5.90
0.25	7.60	3.85	6.30
0.50	8.05	3.95	6.65
1.00	8.30	4.20	7.00
1.50	8.55	4.40	7.30
2.00	8.80	4.60	7.50
2.50	8.90	4.75	7.60
3.00	9.10	4.90	7.70
3.50	9.20	5.00	7.95
4.00	9.40	5.20	8.20
4.50	9.50	5.35	8.50
5.00	9.60	6.00	8.85

(A) = 50 ml of 0.01M β-Alanine (in the cell)

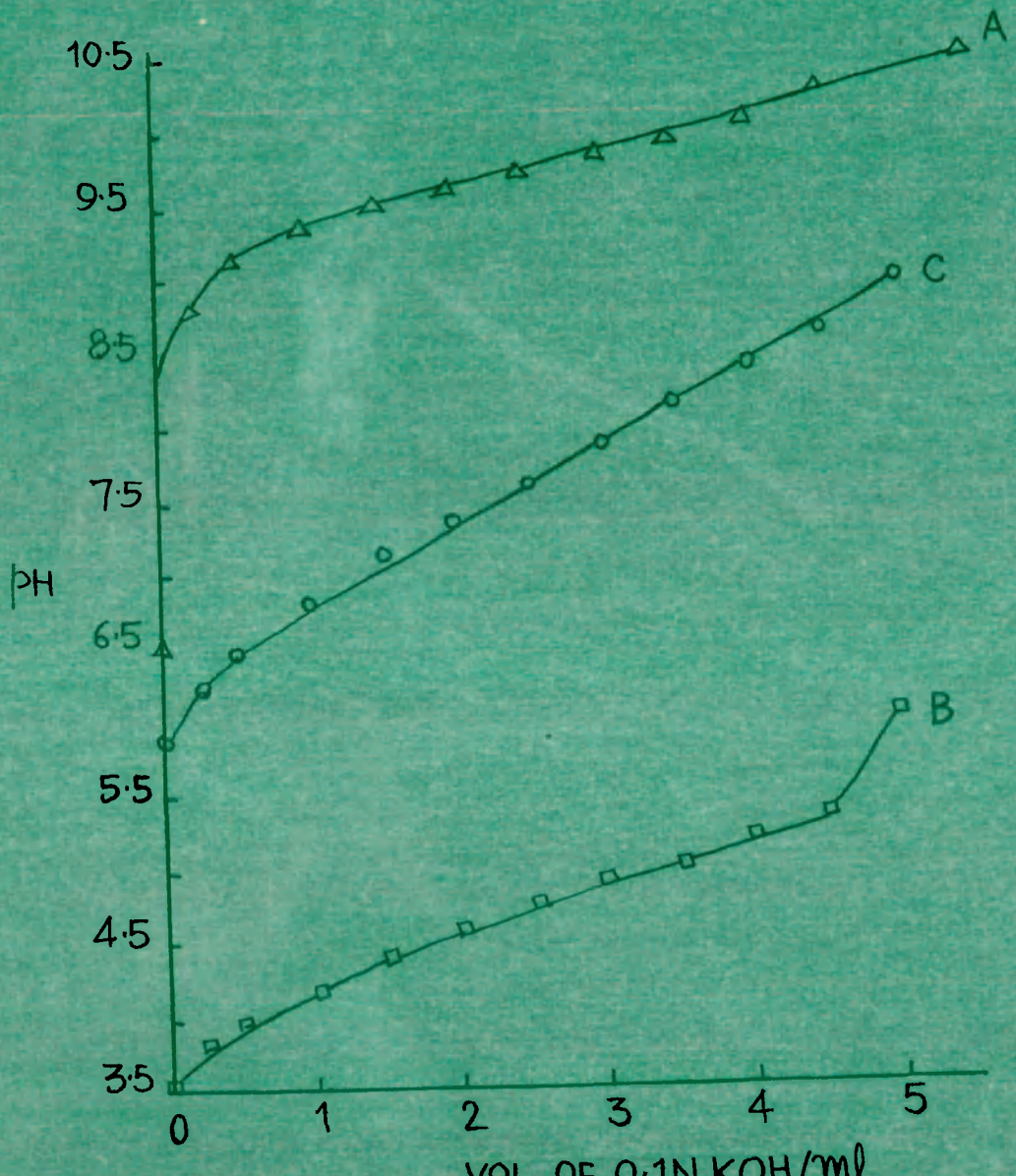
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M β-Alanine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.30 B)

FIGURE NO. 31B

pH-METRIC TITRATIONS.



A = 50 ml OF 0·01M GLYCINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02M GLYCINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 31B

TABLE No.31 B

pH-metric titrations of UO_2^{2+} -Glycine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.50	3.65	5.90
0.25	8.80	3.85	6.25
0.50	9.10	4.00	6.50
1.00	9.35	4.20	6.80
1.50	9.50	4.40	7.15
2.00	9.60	4.60	7.35
2.50	9.70	4.75	7.60
3.00	9.80	4.90	7.85
3.50	9.90	5.00	8.15
4.00	10.00	5.20	8.40
4.50	10.25	5.35	8.60
5.00	10.40	6.00	8.95

(A) = 50 ml of 0.01M Glycine (in the cell)

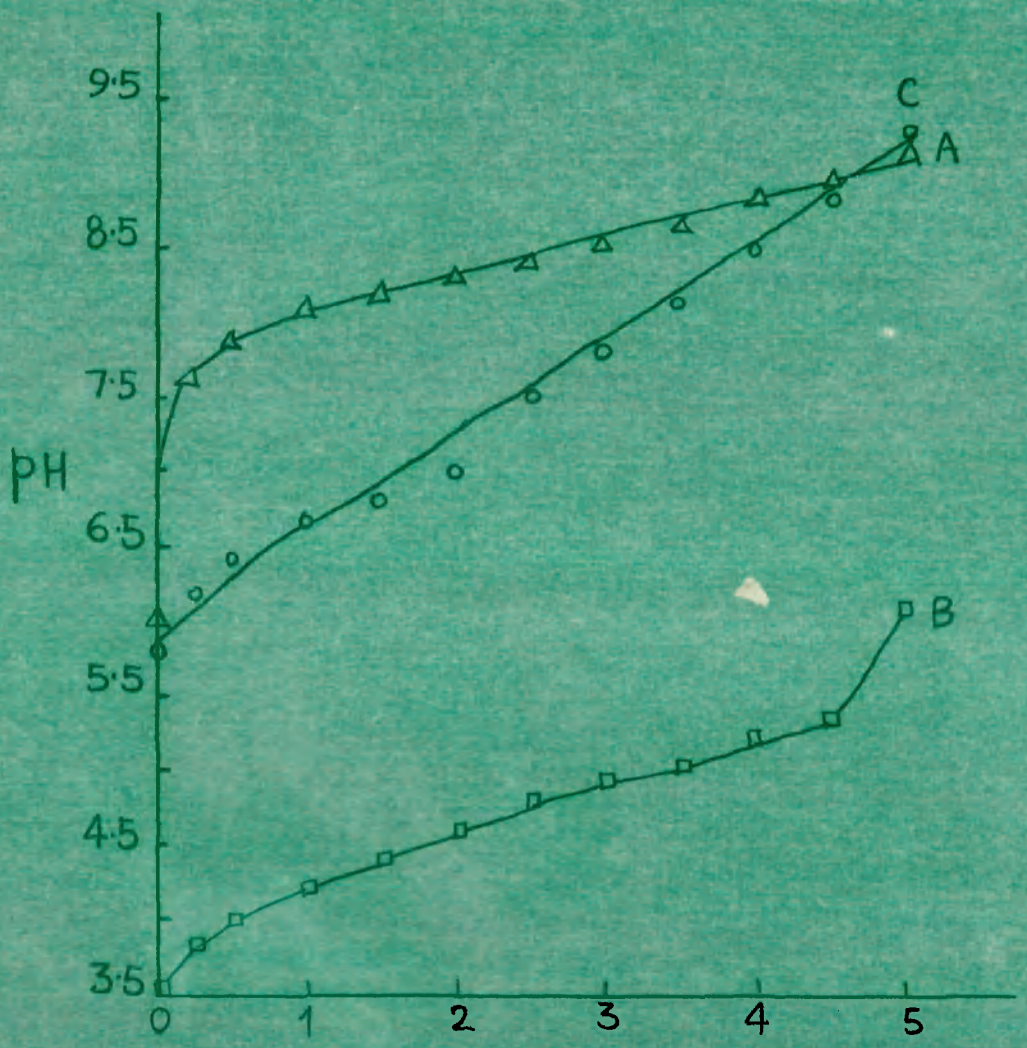
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M Glycine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.31 B)

FIGURE NO. 32 B

PH-METRIC TITRATIONS



VOL. OF 0·1N KOH/ml

A = 50 ml OF 0·01M DL-VALINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02M DL-VALINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 32 B

T A B L E No.32 B

pH-metric titrations of UO_2^{2+}-DL-Valine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.00	3.65	5.85
0.25	7.60	3.85	6.20
0.50	7.90	4.00	6.45
1.00	8.10	4.20	6.70
1.50	8.20	4.40	7.05
2.00	8.30	4.60	7.25
2.50	8.40	4.75	7.55
3.00	8.50	4.90	7.80
3.50	8.60	5.00	8.10
4.00	8.80	5.20	8.45
4.50	8.90	5.30	8.80
5.00	9.10	6.05	9.25

(A) = 50 ml of 0.01M DL-Valine (in the cell)

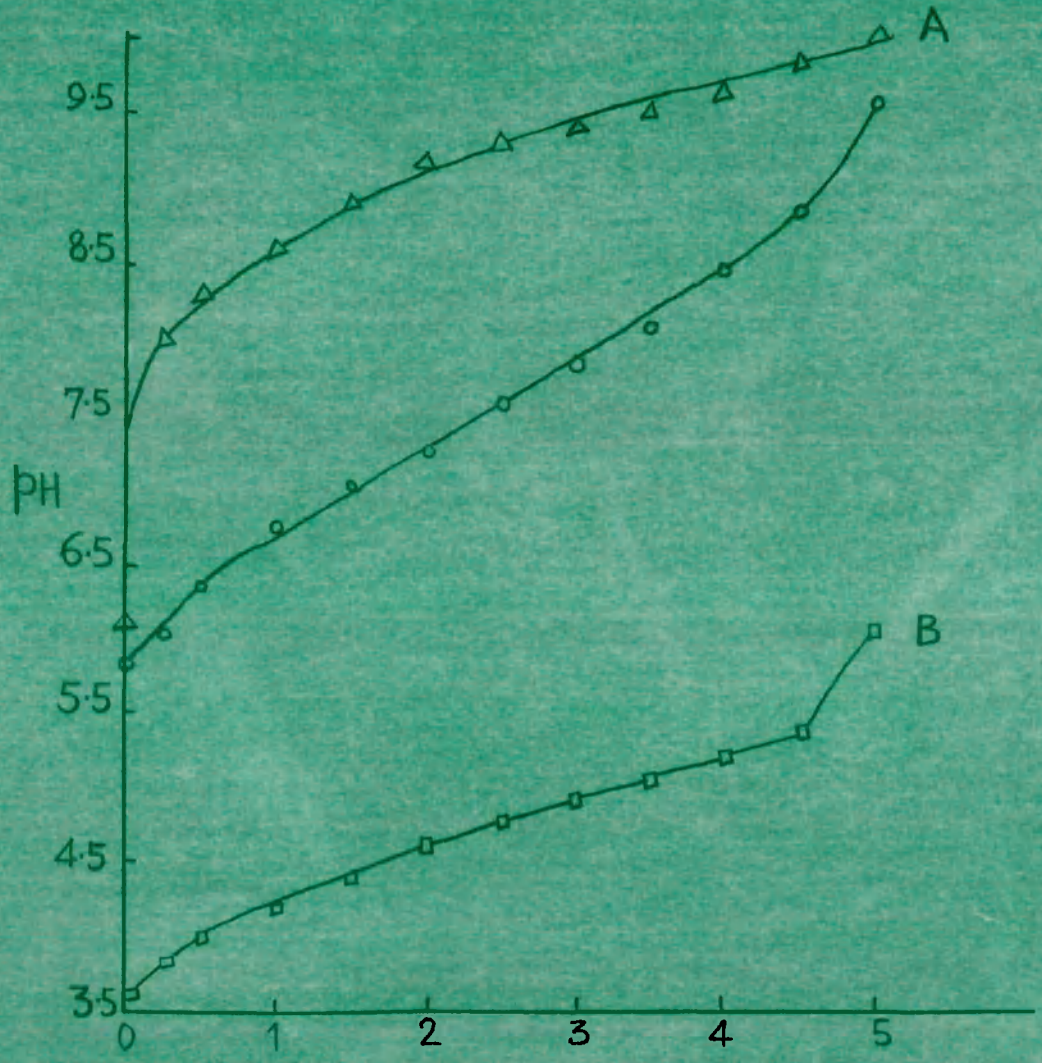
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M DL-Valine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.32 B)

FIGURE NO. 33B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-PROLINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02M L-PROLINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 33B

T A B L E No.33 B

pH-metric titrations of UO_2^{2+}-L-Proline system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.10	3.65	5.80
0.25	8.00	3.85	6.00
0.50	8.30	4.00	6.35
1.00	8.60	4.20	6.70
1.50	8.90	4.40	7.05
2.00	9.20	4.60	7.25
2.50	9.30	4.75	7.55
3.00	9.40	4.90	7.80
3.50	9.50	5.00	8.05
4.00	9.60	5.20	8.45
4.50	9.80	5.35	8.85
5.00	10.00	6.00	9.30

(A) = 50 ml of 0.01M L-Proline (in the cell)

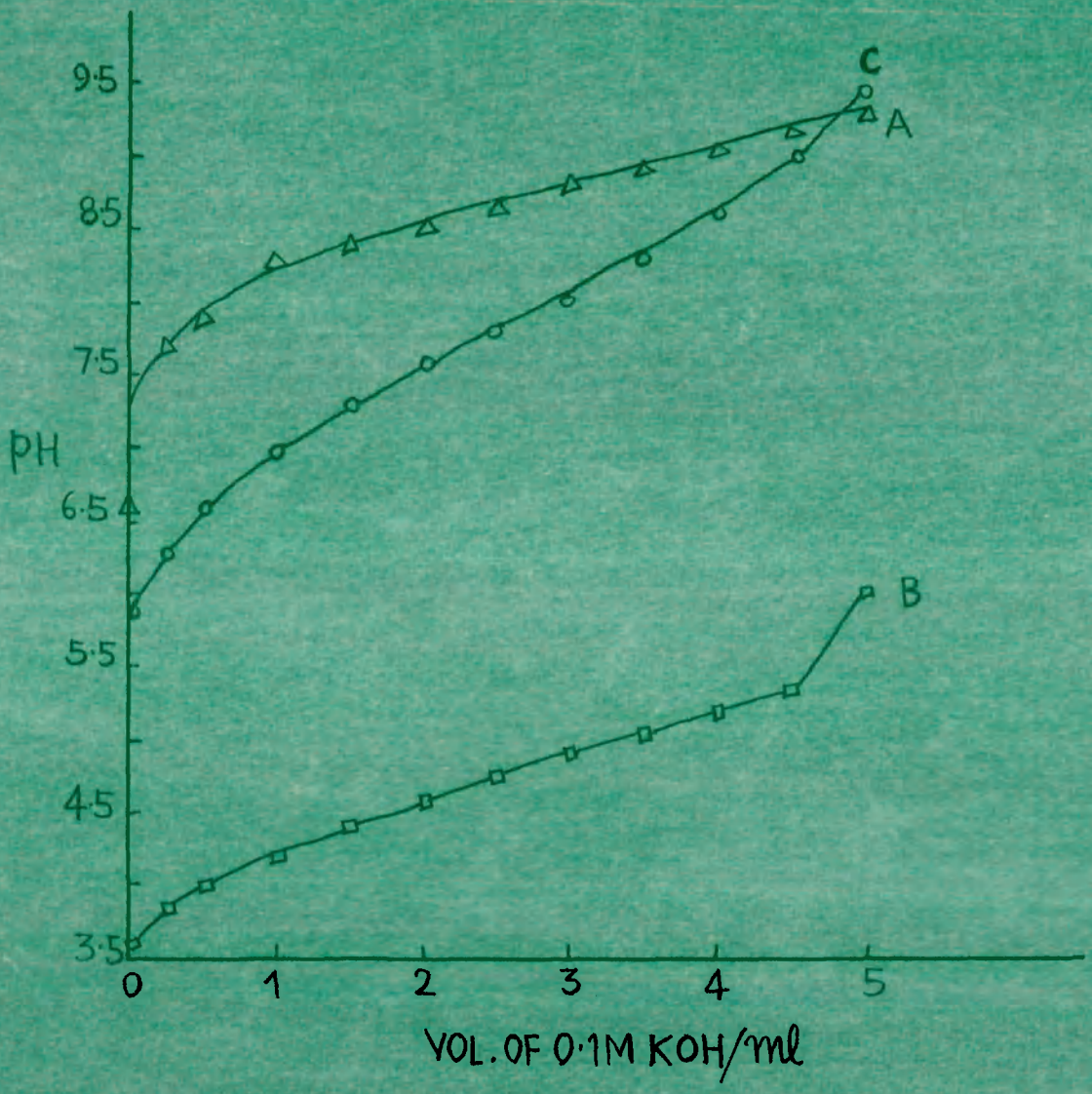
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M L-Proline + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.33 B)

FIGURE NO. 34B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M L-LEUCINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02 M L-LEUCINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 34b

T A B L E No.34 B

pH-metric titrations of UO_2^{2+}-L-Leucine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	6.60	3.65	5.90
0.25	7.70	3.85	6.30
0.50	7.90	4.00	6.65
1.00	8.30	4.20	7.00
1.50	8.40	4.40	7.30
2.00	8.55	4.60	7.60
2.50	8.65	4.75	7.80
3.00	8.80	4.90	8.00
3.50	8.90	5.00	8.30
4.00	9.05	5.20	8.60
4.50	9.15	5.35	9.00
5.00	9.30	6.00	9.40

(A) = 50 ml of 0.01M L-Leucine (in the cell)

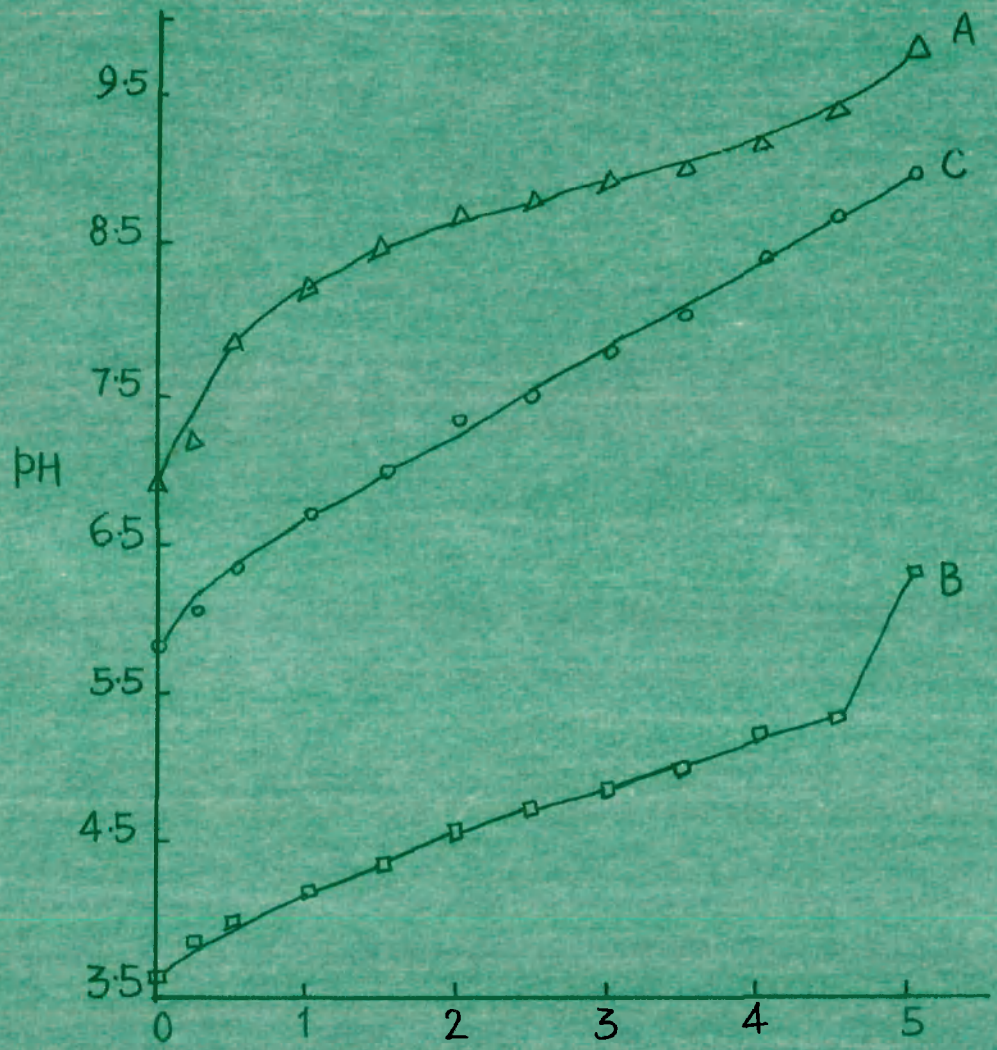
(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M L-Leucine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.34 B)

FIGURE NO. 35 B

pH-METRIC TITRATIONS



A = 50 ml OF 0·01M DL - α - ALANINE (IN THE CELL)

B = 50 ml OF 0·005M UO_2SO_4 (IN THE CELL)

C = 25 ml OF 0·02M DL - α - ALANINE + 25 ml OF 0·01M UO_2SO_4 (IN THE CELL)

VIDE TABLE NO. 35B

T A B L E No.35 B

pH-metric titrations of UO_2^{2+}-DL-α-Alanine system

0.1N KOH (ml)	pH(A)	pH(B)	pH(C)
0.00	5.90	3.65	5.85
0.25	7.20	3.85	6.05
0.50	7.85	4.00	6.35
1.00	8.20	4.20	6.70
1.50	8.50	4.40	7.00
2.00	8.70	4.60	7.35
2.50	8.80	4.75	7.50
3.00	8.90	4.90	7.80
3.50	9.00	5.00	8.05
4.00	9.20	5.25	8.40
4.50	9.40	5.35	8.70
5.00	9.80	6.35	9.00

(A) = 50 ml of 0.01M DL-α-Alanine (in the cell)

(B) = 50 ml of 0.005M Uranyl Sulphate(in the cell)

(C) = 25 ml of 0.02M DL-α-Alanine + 25 ml of 0.01M Uranyl Sulphate (in the cell)

(Vide Fig. No.35 B)

T A B L E No.28 C

pH-metric titration of L-Asparagine (0.01M ; pK_a = 8.86) and Uranyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.35	0.10	-4.5222	3.5656	xx
0.50	6.60	0.20	-4.2958	3.6883	xx
1.00	6.80	0.40	-4.1445	3.9542	xx
1.50	7.15	0.57	-3.9495	4.0943	xx
2.00	7.35	0.74	-3.7108	xx	xx
2.50	7.65	0.93	-3.4808	xx	xx
3.00	7.85	1.11	-3.3615	xx	xx
3.50	8.05	1.26	-3.1615	xx	2.9680
4.00	8.35	1.42	-3.0865	xx	3.0545
4.50	8.70	1.56	-2.7365	xx	3.1843
5.00	9.30	1.81	-2.5910	xx	xx

Mean log K' = 3.82

Mean log K" = 3.06

$\log K_s$ = 3.82 + 3.06 = 6.88 Calculated

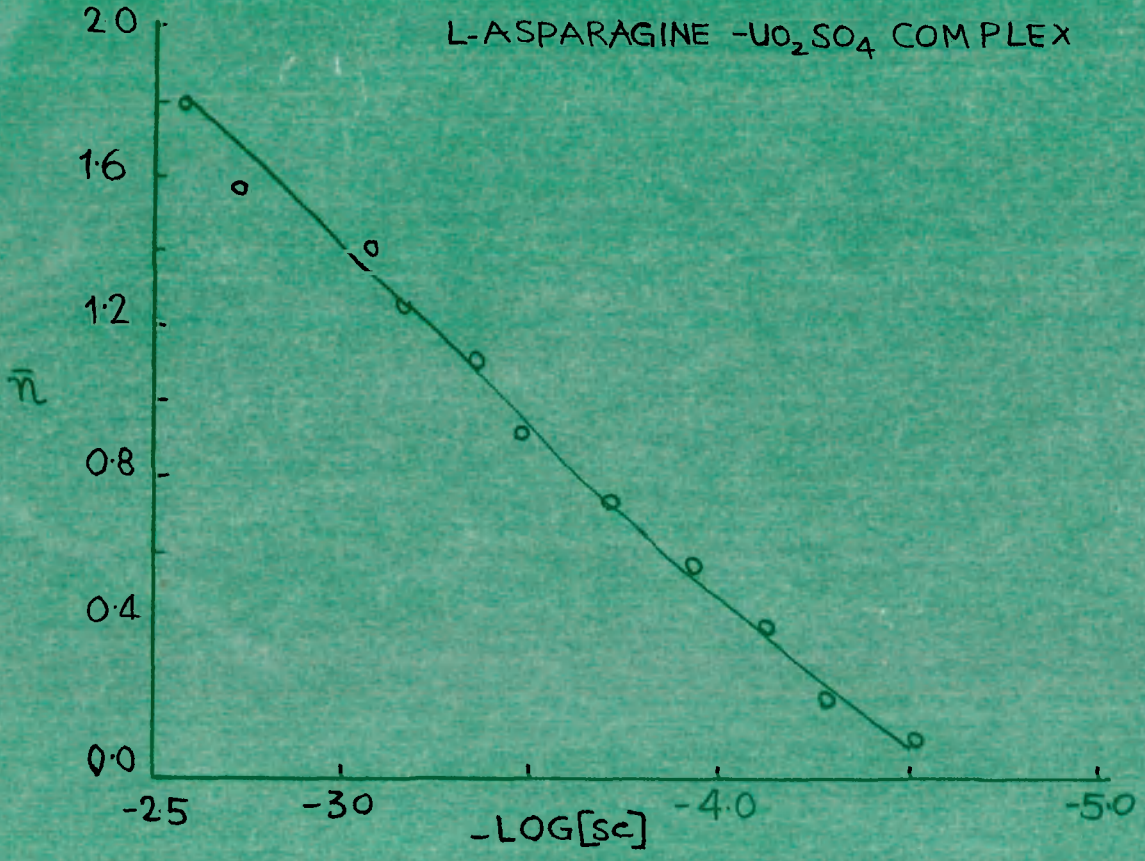
$\log K_s$ 6.85 Graphically.

(Vide Fig. No.28 C)

FIGURE NO. 28C

FORMATION CURVE

L-ASPARAGINE - UO_2SO_4 COMPLEX

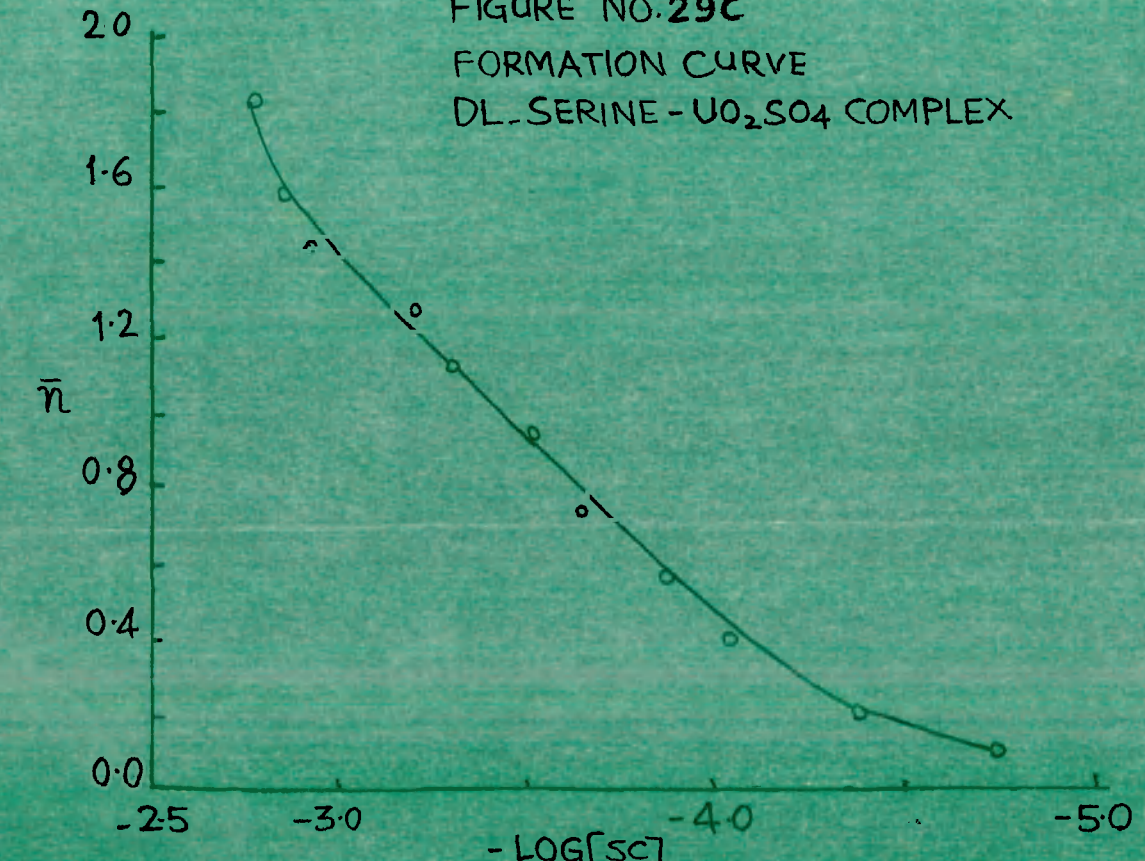


VIDE TABLE NO. 28C

FIGURE NO. 29C

FORMATION CURVE

DL-SERINE - UO_2SO_4 COMPLEX



VIDE TABLE NO. 29C

T A B L E No.29 C

pH-metric titration of DL-Serine (0.01M ; pK_a = 9.15) and Uranyl Sulphate (0.005M); all in 50 ml. $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.40	0.10	-4.7520	3.8156	xx
0.50	6.80	0.20	-4.3958	3.8383	xx
1.00	7.20	0.40	-4.0445	3.8542	xx
1.50	7.40	0.57	-3.8995	4.0443	xx
2.00	7.70	0.74	-3.6608	xx	xx
2.50	7.90	0.93	-3.5308	xx	xx
3.00	8.20	1.11	-3.3115	xx	xx
3.50	8.40	1.26	-3.2112	xx	3.0177
4.00	8.80	1.42	-2.9365	xx	2.9745
4.50	9.05	1.56	-2.8585	xx	2.9654
5.00	9.40	1.81	-2.7910	xx	xx

Mean log K' = 3.88

Mean log K" = 2.98

$\log K_s$ = 3.88 + 2.98 = 6.86 Calculated

$\log K_s$ = 6.90 Graphically.

(Vide Fig. No.29 C)

T A B L E NO.30 C

pH-metric titration of β-Alanine (0.01M ; pK_a = 9.87) and Uranyl Sulphate (0.005M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.30	0.10	-6.0722	5.1056	xx
0.50	6.65	0.20	-5.7558	5.1483	xx
1.00	7.00	0.40	-5.4545	5.2642	xx
1.50	7.30	0.57	-5.2095	5.2843	xx
2.00	7.50	0.74	-5.0708	xx	xx
2.50	7.60	0.93	-5.0408	xx	xx
3.00	7.70	1.11	-5.0215	xx	xx
3.50	7.95	1.26	-4.8712	xx	4.6777
4.00	8.20	1.42	-4.7465	xx	4.7145
4.50	8.50	1.56	-4.6185	xx	4.8254
5.00	8.85	1.81	-4.5510	xx	xx

Mean log K' = 5.19

Mean log K" = 4.73

$\log K_s$ = 5.19 + 4.73 = 9.92 Calculated

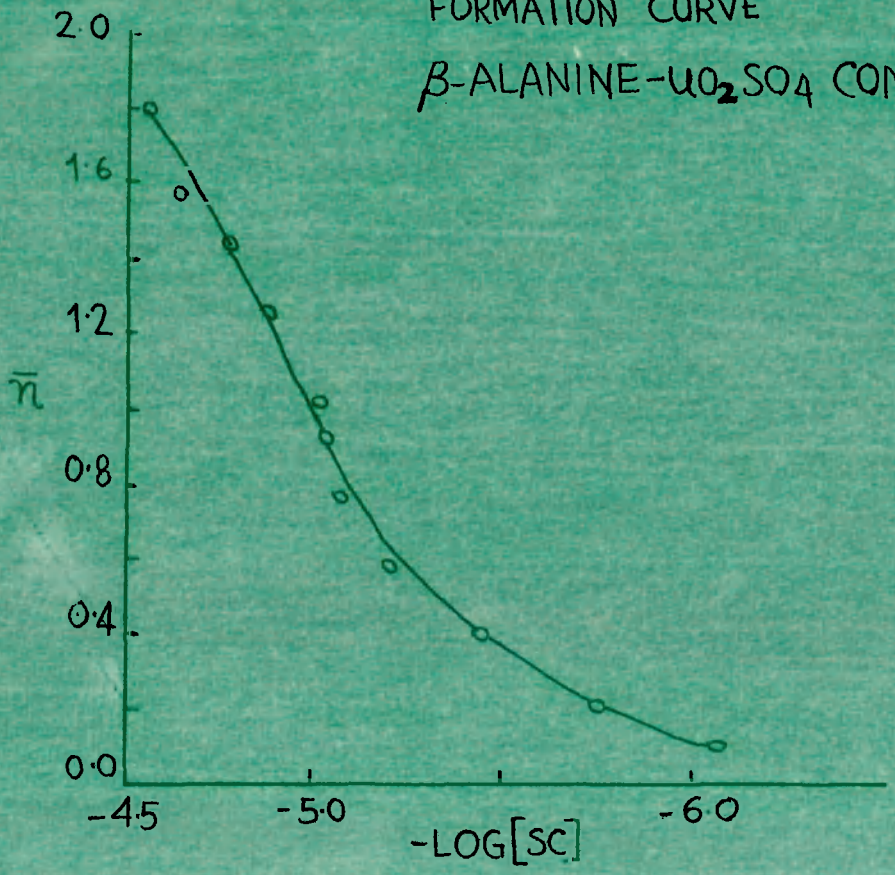
$\log K_s$ = 9.90 Graphically.

(Vide Fig. No.30 C)

FIGURE NO. 30 C

FORMATION CURVE

β-ALANINE-UO_2SO_4 COMPLEX

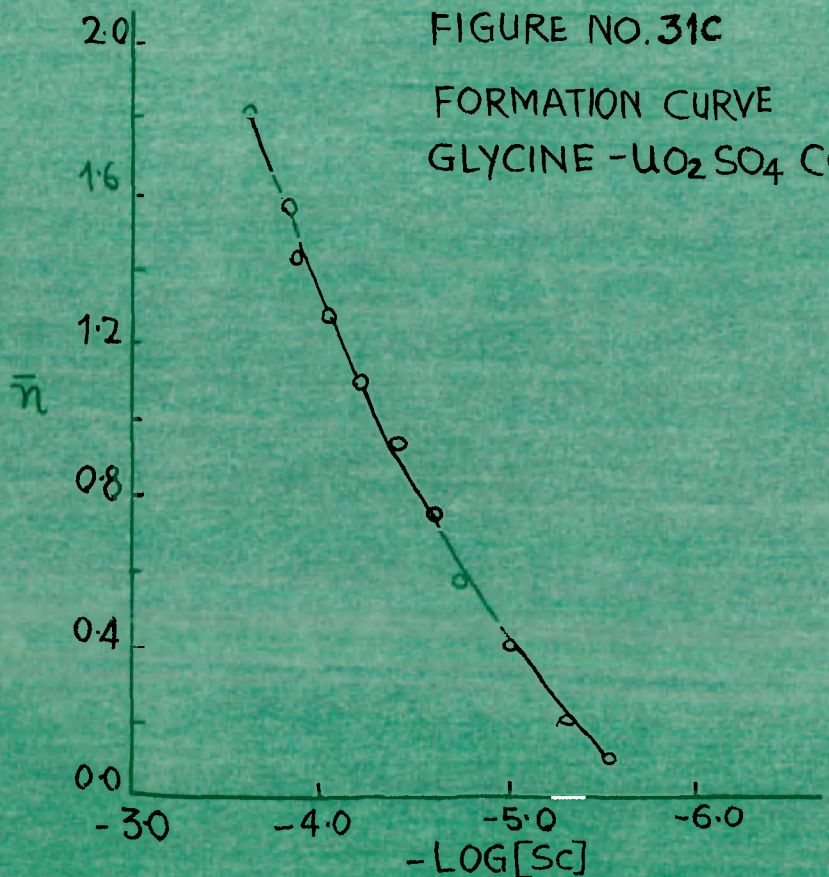


VIDE TABLE NO. 30 C

FIGURE NO. 31C

FORMATION CURVE

GLYCINE -UO_2SO_4 COMPLEX



VIDE TABLE NO. 31C

TABLE No.31 C

pH-metric titration of Glycine (0.01M, pK_a = 9.77) and Uranyl Sulphate(0.005M), all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.25	0.10	-5.5222	4.5656	xx
0.50	6.50	0.20	-5.3158	4.6083	xx
1.00	6.80	0.40	-5.0645	4.7742	xx
1.50	7.15	0.57	-4.7695	4.8143	xx
2.00	7.35	0.74	-4.6308	xx	xx
2.50	7.60	0.93	-4.4508	xx	xx
3.00	7.80	1.11	-4.2815	xx	xx
3.50	8.15	1.26	-4.0812	xx	3.8877
4.00	8.40	1.42	-3.9565	xx	3.9245
4.50	8.60	1.56	-3.9285	xx	4.0354
5.00	8.90	1.81	-3.8610	xx	xx

Mean log K' = 4.68

Mean log K" = 3.94

log K_s = 4.68 + 3.94 = 8.62 Calculated

log K_s = 8.65 Graphically.

(Vide Fig. No.31 C)

T A B L E No.32 C

pH-metric titration of DL-Valine (0.01M ; pK_a = 9.71) and Uranyl Sulphate(0.005M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.20	0.10	-5.5122	4.5556	xx
0.50	6.45	0.20	-5.4058	4.6983	xx
1.00	6.70	0.40	-5.1045	4.9143	xx
1.50	7.05	0.57	-4.8095	4.9543	xx
2.00	7.25	0.74	-4.6708	xx	xx
2.50	7.55	0.93	-4.4408	xx	xx
3.00	7.80	1.11	-4.2715	xx	xx
3.50	8.10	1.26	-4.0712	xx	3.8777
4.00	8.45	1.42	-3.8465	xx	3.8145
4.50	8.80	1.56	-3.6685	xx	3.7754
5.00	9.25	1.81	-3.5010	xx	xx

Mean log K' = 4.78

Mean log K" = 3.81

$\log K_s$ = 4.78 + 3.81 = 8.59 Calculated

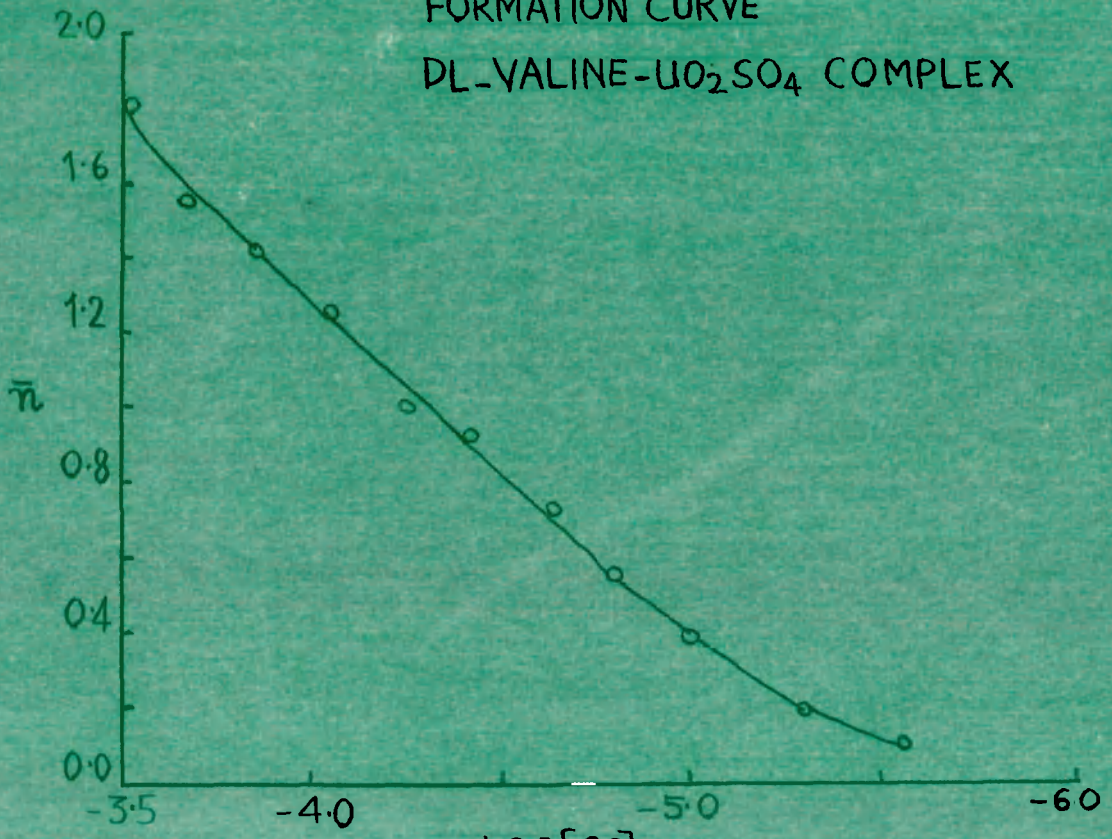
$\log K_s$ = 8.60 Graphically.

(Vide Fig. No.32 C)

FIGURE NO. 32C

FORMATION CURVE

DL-VALINE-UO_2SO_4 COMPLEX

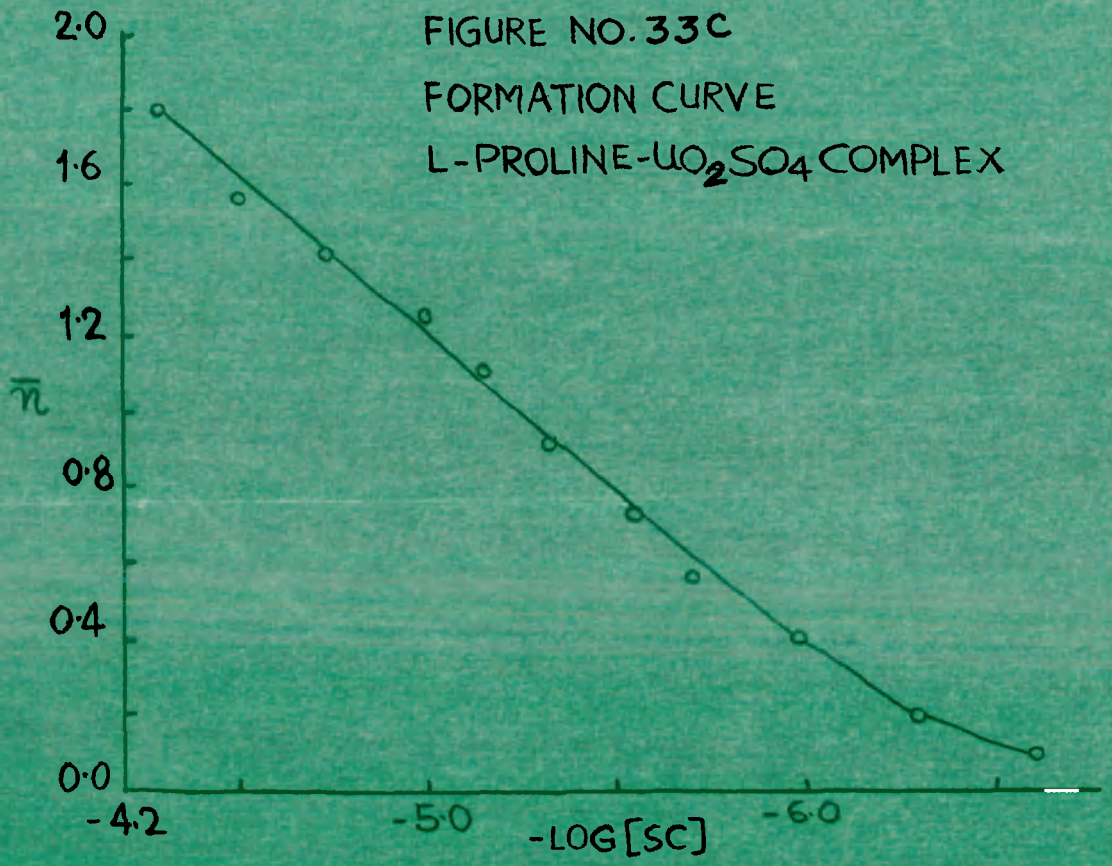


VIDE TABLE NO. 32C

FIGURE NO. 33C

FORMATION CURVE

L-PROLINE-UO_2SO_4 COMPLEX



VIDE TABLE NO. 33C

T A B L E No.33 C

pH-metric titration of L-Proline (0.01M ; pK_s = 10.60) and Uranyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log[Sc]	log K'	log K"
0.00	5.80	xx	xx	xx	xx
0.25	6.00	0.10	-6.6022	5.6456	xx
0.50	6.35	0.20	-6.2958	5.6882	xx
1.00	6.70	0.40	-5.9845	5.7942	xx
1.50	7.05	0.57	-5.6995	5.8443	xx
2.00	7.25	0.74	-5.5608	xx	xx
2.50	7.55	0.93	-5.3302	xx	xx
3.00	7.80	1.11	-5.1615	xx	xx
3.50	8.05	1.26	-5.0112	xx	4.8177
4.00	8.45	1.42	-4.7365	xx	4.7045
4.50	8.85	1.56	-4.5085	xx	4.6954
5.00	9.30	1.81	-4.2910	xx	xx

Mean log K' = 5.73

Mean log K" = 4.73

$\log K_s$ = 5.73 + 4.73 = 10.46 Calculated

$\log K_s$ = 10.45 Graphically.

(Vide Fig. No.33 C)

T A B L E No.34 C

pH-metric titration of L-Leucine (0.01M ; pK_a = 9.92) and Uranyl Sulphate (0.005M) ; all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.90	xx	xx	xx	xx
0.25	6.30	0.10	-5.6222	4.6656	xx
0.50	6.65	0.20	-5.3158	4.7083	xx
1.00	7.00	0.40	-5.0145	4.8245	xx
1.50	7.30	0.57	-4.7695	4.9143	xx
2.00	7.60	0.74	-4.5308	xx	xx
2.50	7.80	0.93	-4.4008	xx	xx
3.00	8.00	1.11	-4.2815	xx	xx
3.50	8.30	1.26	-4.0812	xx	3.8877
4.00	8.60	1.42	-3.9065	xx	3.8745
4.50	9.00	1.56	-3.6785	xx	3.7884
5.00	9.40	1.81	-3.5610	xx	xx

Mean log K' = 4.77

Mean log K" = 3.84

$\log K_s = 4.77 + 3.84 = 8.61$ Calculated

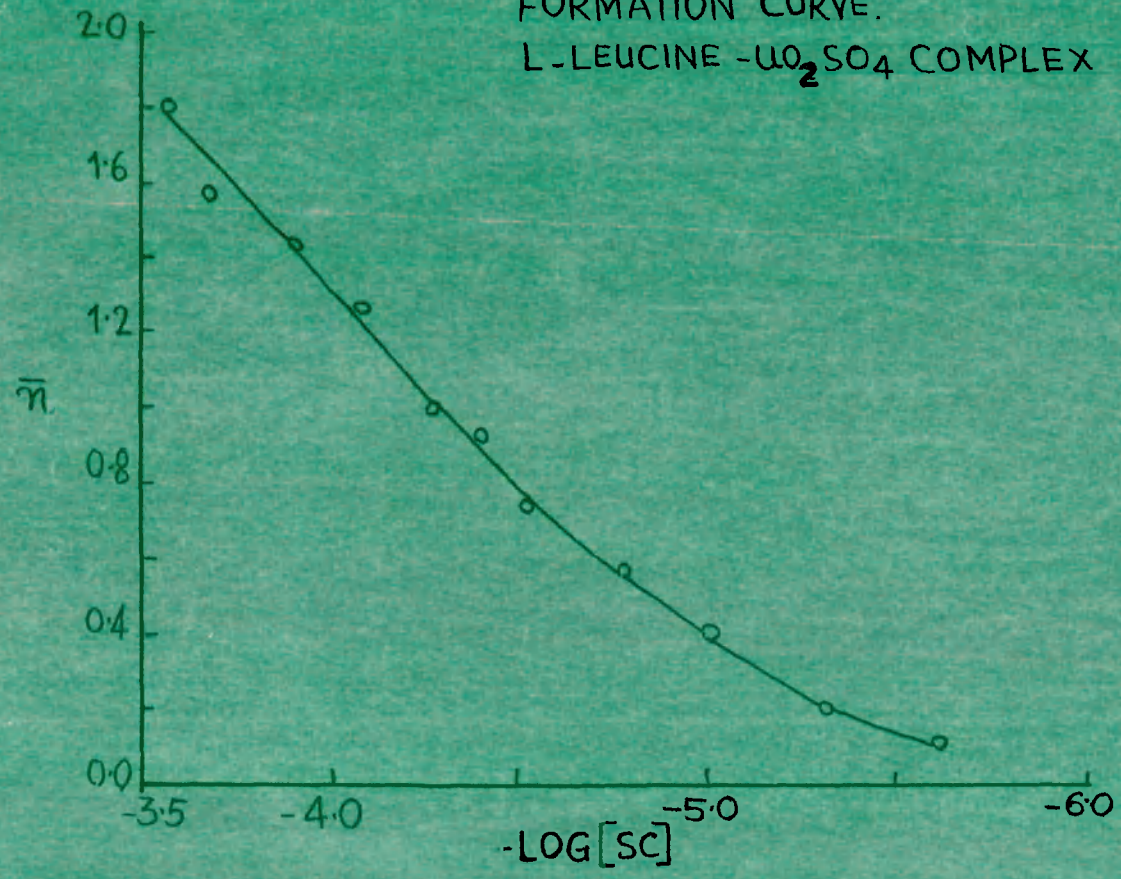
$\log K_s = 8.60$ Graphically.

(Vide Fig. No.34 C)

FIGURE NO. 34C

FORMATION CURVE.

L-LEUCINE - UO_2SO_4 COMPLEX

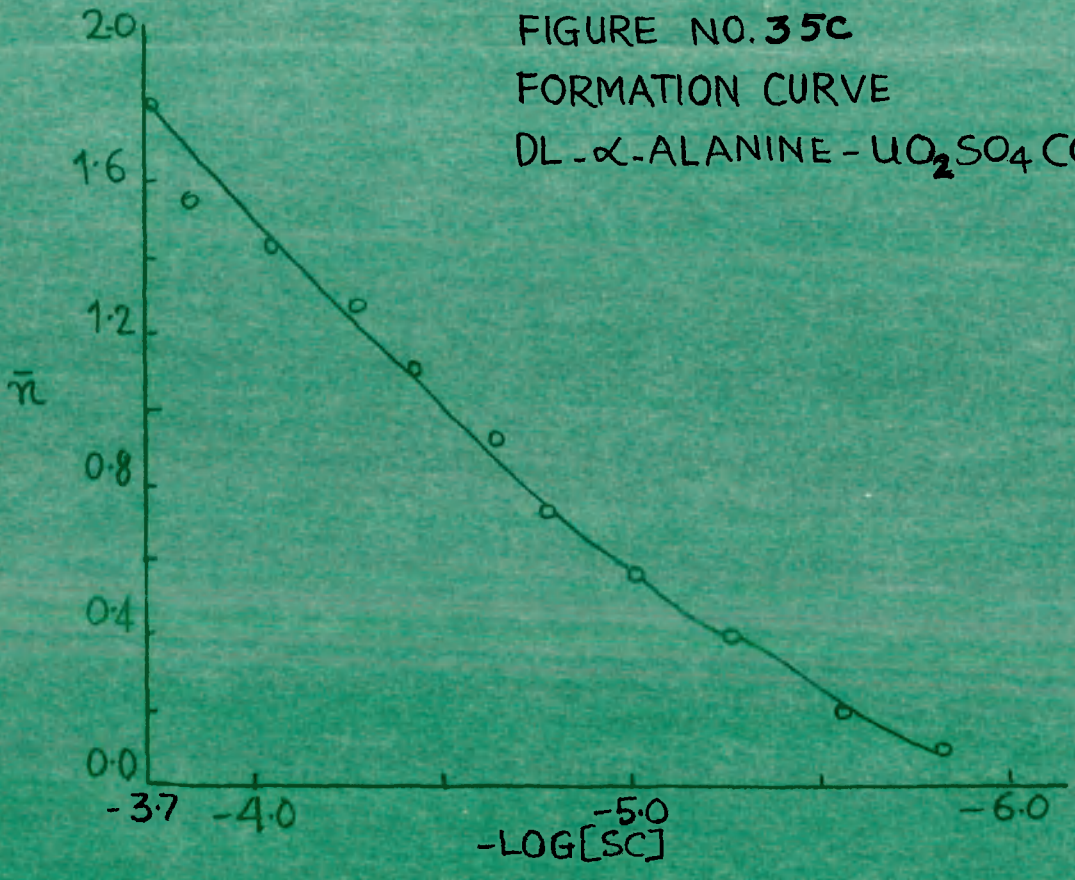


VIDE TABLE NO. 34C

FIGURE NO. 35C

FORMATION CURVE

DL-α-ALANINE - UO_2SO_4 COMPLEX



VIDE TABLE NO. 35C

T A B L E No.35 C

pH-metric titration of DL-α-Alanine(0.01M; pK_a = 9.86) and Uranyl Sulphate (0.005M); all in 50 ml, $[HSc^{\circ}]$ = 0.01.

0.1N KOH (ml)	pH	$\bar{n}$	-log [Sc]	log K'	log K"
0.00	5.85	xx	xx	xx	xx
0.25	6.05	0.10	-5.8122	4.8556	xx
0.50	6.35	0.20	-5.5558	4.9483	xx
1.00	6.70	0.40	-5.2545	5.0642	xx
1.50	7.00	0.57	-5.0095	5.1543	xx
2.00	7.35	0.74	-4.7708	xx	xx
2.50	7.50	0.93	-4.6408	xx	xx
3.00	7.80	1.11	-4.4215	xx	xx
3.50	8.05	1.26	-4.2715	xx	4.0777
4.00	8.40	1.42	-4.0465	xx	4.0145
4.50	8.70	1.56	-3.8185	xx	3.9254
5.00	9.00	1.81	-3.7010	xx	xx

Mean log K' = 5.00

Mean log K" = 4.00

$\log K_s$ = 5.00 + 4.00 = 9.00 Calculated

$\log K_s$ = 9.00 Graphically.

(Vide Fig. No.35 C)

T A B L E No.36

Comparison between the values of logarithm of stability constants (log $K_s/mol^2\ L^{-2}$) for Cr^{2+}, VO^{2+}, Ti^{3+} and UO_2^{2+}-amino-acids systems.

Temp. 25°C

	Chromium(II) Chloride		Vanadyl Sulphate		Titanous Chloride		Uranyl Sulphate	
	Calculated	Graphically	Calculated	Graphically	Calculated	Graphically	Calculated	Graphically
L-asparagine	6.97	6.92	6.95	6.90	7.25	7.20	6.88	6.85
β- alanine	9.89	9.86	9.77	9.80	7.72	7.70	9.92	9.90
DL-α-alanine	8.76	8.72	8.75	8.70	8.53	8.50	9.00	9.00
Glycine	9.05	9.02	xx	xx	8.52	8.50	8.62	8.65
L - proline	10.35	10.30	10.33	10.30	10.08	10.05	10.46	10.45
L - Leucine	xx	xx	9.08	9.10	8.55	8.50	8.61	8.60
DL- serine	7.21	7.20	7.54	7.50	7.60	7.60	6.86	6.90
DL-valine	8.68	8.70	8.65	8.65	8.16	8.20	8.59	8.60
DL-Methionine	7.32	7.30	xx	xx	xx	xx	xx	xx
Cysteine	9.77	9.80	xx	xx	xx	xx	xx	xx
Taurine	7.06	7.02	xx	xx	xx	xx	xx	xx
DL-Leucine	8.42	8.40	xx	xx	xx	xx	xx	xx

RESULTS AND DISCUSSION

The compositions of the complexes, formed by the interaction of various aminoacids such as glycine, DL-α-alanine, β-alanine, L-asparagine, L-leucine, L-proline, DL-valine, DL-serine, DL-methionine, cysteine and taurine with chromium(II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(IV) sulphate, were determined by the electrometric methods. The composition of Cr(II) complex was determined potentiometrically, whereas with other metallic ions conductometric titration method was used.

Chromium(II) chloride forms 1:1 complexes with the above mentioned aminoacids as evident from the potentiometric titration curves (figures and tables 2A to 12A). From the conductometric titration curves a ratio 1:1 was established for vanadyl (figures and tables 21A to 27A), uranyl (figures and tables 28A to 35A), and titanous(figures and tables 13A to 20A) complexes with above mentioned aminoacids, but excluding those containing sulphur e.g., DL-methionine, cysteine and taurine. The latter compounds do not show any reactivity towards metal ions concerned, but with the exception of Cr^{2+} ion at ordinary temperature.

The pH-metric titrations were performed in order to evaluate the stability constants of the various complexes formed by the union of metal ions and aminoacids. These titrations were performed in triplicate for each aminoacid in the order: (a) aminoacid (0.01M), (b) metal salt (0.005M) and (c) metal salt and aminoacid (total concentration 0.005M and 0.01M, respectively) using 0.1N KOH as titrant. The pH-metric titration curves (figures and tables 2B to 35B) show appreciable shifts, thus indicating formation of complexes with aminoacids. The complex formation constant K_s was evaluated by the Bjerrum's method[3] simplified by Albert[4] for aminoacid systems.

The stepwise complex formation between a divalent metal (M^{2+}) and aminoacid resulting in the formation of species MA^+ and MA_2 may be explained as,

$$NH_3^+ ACOO^- + M^{2+}Cl_2^- \underset{}{\overset{K'}{\rightleftharpoons}} [MNH_2 ACOO^-]^+ Cl^-$$

$$NH_3^+ ACOO^- + [M\ NH_2ACOO^-] \overset{K''}{\rightleftharpoons} [M\ (NH_2ACOO^-)_2]^o + H^+ + Cl^-$$

Assuming the ionization of the amino group as $NH_3^+ACOO^- \xrightarrow{Ka} NH_2ACOO^- + H^+$, the values of first and second equilibrium constants K' and K" may be given as,

$$K' = \frac{[MA^+]}{[M][A^-]} \text{ ----- (I)}, \quad K'' = \frac{[MA_2]}{[MA^+][A^-]} \text{ ------ (II)}$$

and the overall stability constant $K_s = K'\ K'' = \frac{[MA_2]}{[M][A^-]^2}$ ---(III)

As complex formation proceeds, H^+ ions are liberated and the measurements of the concentration of these ions provide a mean of estimating the extent of complex formation.

As the concentration of free metallic ion is not measured by this method, the values of K' and K" can be rewritten as

$$K' = \bar{n} / (1-\bar{n}) [Sc] \quad .... \quad (IV)$$

and

$$K'' = \bar{n} - 1 / (2-\bar{n}) [Sc] \quad .... \quad (V)$$

where $[Sc]$ is the concentration of chelating species and $\bar{n}$ is the average number of mols. of complex forming agent bound by one atom of the metal.

Values of log $[Sc]$ could be obtained from the following relation which holds good for the simple mono-amino monocarboxylic acid between pH 3 and 11.

$$\log [Sc] = (pH-pK_a) + \log \left\{ [HSc^o] - [KOH] \right\} \quad ... \quad (VI)$$

where $[HSc^o]$ is the concentration of complex forming agent before the metal is added. $[KOH]$ is the concentration of potassium hydroxide which would be present if the complex forming agent and metal were absent, and pK_a is the ionization constant of the equilibria:

$$NH_3^+ ACOO^- \rightleftharpoons NH_2ACOO^- + H^+$$

The values of $\bar{n}$ can be determined by the greatly simplified equation,

$$\bar{n} = \frac{2\,[KOH]}{[HSc^{O}]} \qquad \ldots\ldots \quad (VII)$$

$$\text{also,} \quad \bar{n} = \frac{[MA^{+}] + 2\,[MA_2]}{[M] + [MA^{+}] + [MA_2]} \qquad \ldots\ldots \quad (VIII)$$

when $\bar{n} = 1, [MA^{+}] + 2[MA_2] = [M] + [MA^{+}] + [MA_2]$

hence $[M] = [MA_2]$ and as $K_s = \frac{[MA_2]}{[M]\,[Sc]^2}$

$$\text{or} \quad K_s = \frac{1}{[Sc]^2} \qquad \ldots\ldots \quad (IX)$$

$$\text{or} \quad \log K_s = 2 \log [Sc]$$

By titrating each aminoacid in the presence of various metallic ions, pH-values were obtained for each addition of alkali and from these readings values for [Sc], and $\bar{n}$ were calculated from (VI) and (VII), respectively. The values of K' and K" were calculated from (IV) and (V), respectively.

In tables (2C to 12C) Cr^{2+}, (13C to 20C) Ti^{3+}, (21C to 27C) VO^{2+} and (28C to 35C) UO_2^{2+}, are given the values of pH, $\bar{n}$, - log [Sc], log K' and log K" for various metal-amino-acid systems. From the plots of -log [Sc] versus $\bar{n}$, (formation curves) given in figures 2C to 35C, for various metals

aminoacid systems, the values of -log[Sc] have been evaluated at $\bar{n} = 1$, subsequently the values of log K_s by applying the relation (IX). The calculated values of log K_s were determined by the addition of log K' and K", the latter were calculated from equations (IV) and (V). The values of K_s determined graphically as well as calculated from the above relations are given in table No.36.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. From the values of log K_s summarised in table no.36, it appears that the order of stabilities of the metal ions studied can not be generalised for the aminoacids used in the complex formation studies. With respect to the aminoacid systems the orders of stabilities can be put into three categories namely, (i) aminoacid complexes containing β-alanine, DL-α-alanine and L-proline, where the order of stability is: $UO_2^{2+} > VO^{2+} \approx Cr^{2+} > Ti^{3+}$, (ii) a reverse order that of (i), comprising L-asparagine, and DL-serine, where metals follow the order: $Ti^{3+} > Cr^{2+} \approx VO^{2+} > UO_2^{2+}$ and (iii) in which metals follow the order in between (i) and (ii) e.g., $VO^{2+} \approx Cr^{2+} > UO_2^{2+} > Ti^{3+}$ includes aminoacids such as L-leucine and DL-valine. An important generalisation from this categorisation is that the aminoacids belonging

to the first category have highest pK_a's values e.g., L-proline (10.68), β-alanine (10.66) and DL-α-alanine (9.97), whereas the two aminoacids L-asparagine and DL-serine belonging to (ii) have the lowest pK_a's values. The rest of the aminoacids have pK_a's values in between (i) and (ii). However, the values of stability constant for VO^{2+}-glycine complex, unfortunately, could not be reliablely evaluated and for the rest of the three metals the order is: $Cr^{2+} > UO_2^{2+} > Ti^{3+}$. The stabilities of Cr^{2+} and VO^{2+} complexes are almost the same for each of the aminoacid complex studied.

The stability order in the complexes of VO^{2+}, UO_2^{2+}, Ti^{3+} and Cr^{2+} in general, is: L-proline > β-alanine > DL-α-alanine > glycine > L-leucine > DL-valine > DL-serine > L-asparagine, which is roughly the same as that of pK_a's order of the amino acids e.g., L-proline, the highest (10.68) and L-asparagine, the lowest (8.85).

The 1:1 complexes of chromium(II) chloride with sulphur containing aminoacids such as cysteine, methionine and taurine follow the stability order: cysteine > methionine > taurine, which is roughly the same as that of the order of pK_a's values of cysteine (10.28), methionine (9.34), and taurine (9.08). Comparing the values of stability constants of these sulphur containing aminoacids with those of non-sulphur containing aminoacids, some interesting inferences

may be drawn regarding the bonding in sulphur containing aminoacids complexes. The cysteine complex has log K' and log K_s values of 5.16 and 9.77, respectively, whereas the corresponding values for glycine and DL-∝-alanine are 5.02 & 9.05 and 4.84 & 8.36, respectively. The higher stability of cysteine complex in comparison to the corresponding non-sulphur containing aminoacid complexes indicates the involvement of sulphur in coordination. On comparing the stability constants of cysteine with those of taurine, an amino sulphonic acid, the K' and K_s values of the former are 5.16 & 9.77 and that of the latter 4.20 & 7.06. The higher K' and K_s values for cysteine in comparison to glycine and taurine complexes clearly indicate that the bonding takes place at COO^-, $-NH_2$ and -S- coordination sites present in the cysteine. The nature of the bonding in methionine complex can be very well understood by comparing the K' and K_s values of methionine (4.32), leucine (4.63,8.42) and taurine (4.20, 7.06). The stability of methionine complex is lower than leucine but slightly higher than that of taurine, which clearly indicates coordination through NH_2 and COOH groups and there is no involvement of S atom present in the substituted carbon chain. Another factor in favour of this formulation is the presence of-S- in the long chain of carbon atoms quite far from the adjacent amino and

carboxylic groups. The potentiometric and pH-metric studies, carried out to determine the composition and stability of the aminoacid complexes, indicate a combining ratio of 1:1 for metal and aminoacid. The values of stability constants computed from the formation curves are found to be influenced by several factors, namely (1) the pK_a of the aminoacid: the stability of aminoacid complexes increases with increase in pK_a and follows the order: L-proline > β-alanine > DL-α-alanine > glycine > DL-valine > DL-serine > L-asparagine which is almost the same as the pK_a's order in aminoacids, (ii) nature of the metal:uranyl complexes have the highest log K_s values for the aminoacids with largest dissociation constants, whereas Ti^{3+} complexes have the highest log K_s values for aminoacids with lowest dissociation constants, Cr^{2+} and VO^{2+} complexes have almost the same stabilities and the stability constants values of these metals are highest for the aminoacids which have pK_a values in the middle of the series, (iii) the chain length of carbon atoms in the aminoacids and the distance between the carboxylic and amino groups: it is observed that the stability of the aminoacid complexes decreases with increase in the chain length of carbon atoms and the distance between amino and carboxylic groups, this factor is examplified by the lower stabilities of DL-valines, L-leucine and DL-serine

complexes and greater stabilities of proline, glycine and alanine complexes. (iv) the bonding coordination through at COO^- - NH_2 and -SH in Cr(II)- cysteine complex has been demonstrated on comparing the K' and K_s values of cysteine with those of glycine and taurine. The latter two have lower values than cysteine complex. In methionine complex, the coordination through NH_2 and COO^- seems to be the only possibility as derived from the comparison of K' and K_s values of the former with those of leucine and taurine complexes. The values for methionine are lower than leucine but higher than that of taurine.

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C H A P T E R - II:

BEHAVIOUR OF COPPER (I) IODIDE IN AQUEOUS POTASSIUM IODIDE CONTAINING AMINOACIDS.

INTRODUCTION

An interesting aspect of the problem concerning with the metal aminoacid complexes is the study of complex formation on the basis of solubility measurements. The earlier investigators studied the solubility behaviour of metallic salts in aminoacid solutions with complete ignorance about the possibility of complex formation. Thus in 1933, Pailey[1] studied the solubilities of thallous iodate in the presence of various aminoacids in a view to seek a relationship between the dielectric constant of the amino-acid solutions and the solubility of the salt. It was found that a linear relationship existed between the logarithm of the solubility of the salt, and the concentration of aminoacid present, but no influence of dielectric constant was observed. Similarly Keefer, Reiber and Bisson[2], in 1940, reported a linear increase in the solubility of calcium and barium iodates in the presence of increasing amounts of glycine and alanine without giving any indication of the complex formation. Only in the later reports by Keefer and Reiber[3-5], the possibility of complex formation was mentioned on the basis of larger solubility slopes of $AgIO_3$ and $Pb(IO_3)_2$ in solutions of glycine and alanine. The alanine slope was more steeper than that of glycine. The measured dissociation

constants for silver glycinate were $K=5.28 \times 10^{-5}$; for silver alaninate $K = 1.37 \times 10^{-5}$; for lead glycinate $K = 6.7 \times 10^{-6}$, and for lead alaninate $K=3.0 \times 10^{-6}$. According to these data, the silver or lead alaninate complex was more stable (i.e., less dissociated) than the corresponding glycine complexes, the increase in solubility of the salt being a direct measure of the association of the metal with the added anion.

Keefer[5] also studied the solubility of cupric iodate in glycine and alanine solutions, and observed that when cupric iodate was added, an increase in acidity occurred, indicating that a reaction took place which produced H^+ ions. The studies of Keefer and his associates, were followed by Davies and Waind[6], who studied the solubility behaviour of $CaIO_3$ in solution of aminoacids.

Monk[7,a,b,c] made an important contribution in this field and reported the composition, and stability constants of the aminoacid complexes with metal ions, such as Cu^{2+}, Ag^+, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+} and Ca^{2+} in a series of papers appeared in 1951. Monk calculated the dissociation constants of copper(II) complexes with glycine, alanine and glycylglycine, from the results of solubility of cupric iodate in solutions containing an excess of aminoacid and varying amounts of hydrochloric acid and NaOH.

The copper(II)-aminoacid system was further studied by pH-metric titration methods to provide some supporting evidence. He also evaluated the dissociation constants of silver (I) complexes by utilising the solubility data of $AgBrO_3$ and $AgIO_3$ in solution of aminoacids containing NaOH. The values of the stability constants given by Monk for the aminoacid complexes were found to be in good agreement with those found out by potentiometric[8,9] and polarographic methods.[10,11]

Numerous references are available in the chemical literature regarding the complexes of copper (II) salts with aminoacids, and in fact the first systematic study on aminoacid complexes started with the work of Ley[12] on copper(II) complexes with glycine. However, no work has been referred so far in the chemical literature dealing with copper(I) complexes with aminoacids, only the reaction between cysteine and copper(II) salts has been described resulting in the precipitation of cystine and cuprous cysteine.[13]

$$2Cu^{2+} + 2RS \longrightarrow RSSR + 2\ Cu^{+}$$

$$2Cu^{+} + 2RS \longrightarrow 2RSCu$$

Also, Hopkins[14] described the preparation of cysteine cuprous mercaptide by the interaction of cuprous oxide

with cysteine. Perhaps, the greatest single factor which did not stimulate the workers to study the interactions of copper(I) with aminoacids is the insoluble nature of copper (I) salts. The copper (I) halides although insoluble in water, can be made soluble in aqueous halide solutions forming a variety of complex species.[15,16] Keeping in view this character of copper (I) halide to get dissolved in alkali halide solutions, an indirect approach has been made to study the solubility behaviour of copper (I) iodide in aqueous potassium iodide solutions in the presence of various aminoacids.

(i) Solubility of copper (I) iodide in aqueous KI in the presence of aminoacids, such as glycine, L-leucine and L-proline.

(ii) Determination of the composition of the complexes of aminoacids with copper (I) iodide from solubility data.

(iii) Calculation of the solubility product, Ksp and its relationship with the concentration of aminoacid [L].

EXPERIMENTAL

Chemicals:

The aminoacids glycine, L-leucine and L-proline (B.D.H. biologically pure products) were used. Cuprous iodide was prepared by the addition of solid potassium iodide (B.D.H. A.R.) to a solution of cupric sulphate (B.D.H.) and the excess of iodine was removed by passing a current of sulphur dioxide. The white product so obtained was filtered, washed several times with water, alcohol and finally dried with ether, and kept in a desiccator over anhydrous calcium chloride.

Apparatus :

The spectrophotometric measurements were made with a Bausch & Lomb spectronic '20' using the standard cuvettes of 1 cm diameter.

Colorimetric determination of aminoacids:

Aminoacids were estimated[17] spectrophotometrically by using 0.5% ninhydrin in ethanol as a colorimetric reagent. Ninhydrin was added to the solutions containing varying amounts of aminoacids and absorption was taken at 575 m μ (for glycine and L-leucine) and 550 m μ in case of L-proline. Calibration curves between optical density

and the concentration were plotted (Fig. No. 1). Concentrations of the aminoacids in cuprous solutions were determined by using the calibration curve. In case of glycine and L-leucine, the solutions were heated for half an hour over water bath for developing the violet colour. In case of L-proline, the solutions were kept over night for the development of the brown colour. For a particular set all spectrophotometric measurements were carried out in exactly identical conditions and the pH was maintained at about 6.5.

Procedure for the determination of Cu^{+} - contents in aminoacids solutions.

A saturated solution of cuprous iodide in potassium iodide was prepared by dissolving about 10 gms of cuprous iodide in one litre of 2M potassium iodide. The supernatant liquid (saturated solution of cuprous iodide in potassium iodide) was diluted with a standard 2M solution of KI in the following order by decreasing the amount of cuprous iodide solution and increasing the amount of potassium iodide, keeping the total volume (40 ml) constant.

Sample	Vol.of Cu_2I_2	Vol.of 2M KI
1	36 ml	4 ml
2	32 "	8 "
3	28 "	12 "
4	24 "	16 "
5	20 "	20 "
6	16 "	24 "
7	12 "	28 "
8	8 "	32 "
9	4 "	36 "

The second set consisting of the solution prepared according to the above scheme with the exception that for dilution, standard solutions of the aminoacids in 2M potassium iodide were used in place of potassium iodide solution. The cuprous was estimated by diluting the samples with excess of water till all the cuprous was precipitated as Cu_2I_2.

For each aminoacid, calculations were made by considering the contents of the two sets, one with and the other without aminoacid. The difference between the two gives the cuprous consumed in complex formation. The difference in concentration of the aminoacid added to the cuprous solution originally and that obtained from the cuprous solution in the second set gives the concentration of aminoacid bounded to the metal.

T A B L E No.1A

Calibration curve for glycine - Cu_2I_2 system.

λ max = 575 m μ , Temp. 25°C

Conc.of Glycine x 10^{-5}M	Absorption (O.D.)
5.00	0.00
10.00	0.02
15.00	0.04
20.00	0.07
25.00	0.10
30.00	0.125
35.00	0.15
40.00	0.18
45.00	0.205

(Vide Fig. No. 1)

T A B L E No. 1B

Calibration curve for L-proline -Cu_2I_2 system.

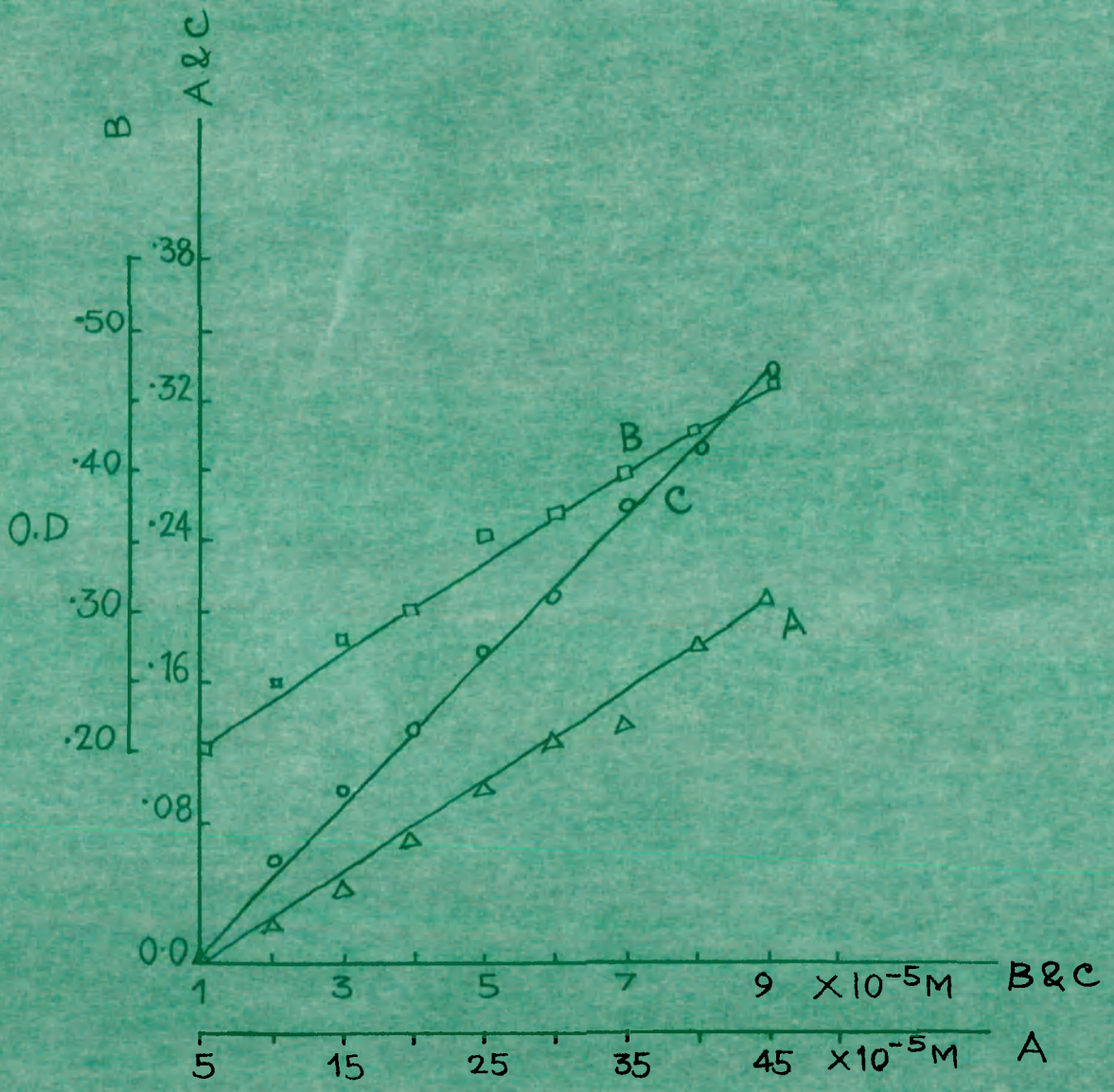
λ max = 550 m μ , Temp. 25°C

Conc.of L-proline x 10^{-5}M	Absorption (O.D.)
1.00	0.20
2.00	0.25
3.00	0.28
4.00	0.30
5.00	0.36
6.00	0.37
7.00	0.39
8.00	0.42
9.00	0.47

(Vide Fig. No. 1)

FIGURE NO.1

CALIBERATION CURVES.



CONCENTRATION OF AMINOACIDS

A= GLYCINE – Cu_2I_2 SYSTEM

B = L-PROLINE – Cu_2I_2 SYSTEM

C = L-LEUCINE – Cu_2I_2 SYSTEM

VIDE TABLE NO.1

TABLE No.1 C

Calibration curve for L-leucine - Cu_2I_2 system

λmax = 575 m μ. Temp. 25°C.

Concentration of L-leucine x 10^{-5}M	Absorption (O.D.)
1.00	0.000
2.00	0.060
3.00	0.095
4.00	0.135
5.00	0.180
6.00	0.225
7.00	0.260
8.00	0.360
9.00	- - -

(Vide Fig. No. 1)

TABLE No.2 A

Solubility data for Cu_2I_2 - glycine complex. Temp. 25°C.

Conc.of Cu_2I_2/10ml with out glycine x 10^{-5}M	Conc.of Cu_2I_2/10ml with glycine x 10^{-5}M	Difference conc.of Cu_2I_2/10ml x 10^{-5}M	Original conc.of glycine/ 10 ml x 10^{-5}M	Conc.of glycine consumed/10ml x 10^{-4}M	Difference in conc.of glycine/10ml x 10^{-4}M	Ratio (Metal: Ligand)
1	2	3	4	5	6	7
0.32	6.72	6.40	5.00	1.31	3.69	1:2
4.09	10.39	6.30	7.50	1.26	6.24	1:2
7.51	12.76	5.25	10.0	1.05	8.95	1:2
11.65	15.85	4.20	12.50	0.84	11.65	1:2
17.29	20.89	3.60	15.00	0.70	14.30	1:2
20.92	24.02	3.10	17.50	0.65	16.85	1:2

TABLE No. 2 B

Solubility data for L-leucine - Cu_2I_2 complex. Temp. 25°C.

Conc.of Cu_2I_2/10ml without L-leucine x 10^{-5}M	Conc.of Cu_2I_2/10ml with L-leucine x 10^{-5}M	Difference in Conc. of Cu_2I_2/10ml x 10^{-5}M	Original Conc.of L-leucine/ 10 ml x 10^{-5}M	Conc.of L-leucine consumed/ 10 ml x 10^{-5}M	Difference in Conc.of L-leucine/ 10 ml x 10^{-5}M	Ratio (Metal: Ligand)
1	2	3	4	5	6	7
4.93	7.03	2.10	5.00	2.40	2.60	1:1
7.45	11.65	4.20	7.50	4.00	3.50	1:1
9.87	14.65	4.78	10.00	4.60	5.40	1:1
12.39	18.69	6.30	12.50	6.20	6.30	1:1
14.68	21.89	7.03	14.00	6.80	7.20	1:1
17.32	24.40	7.08	16.50	6.80	9.70	1:1

TABLE No.2 C

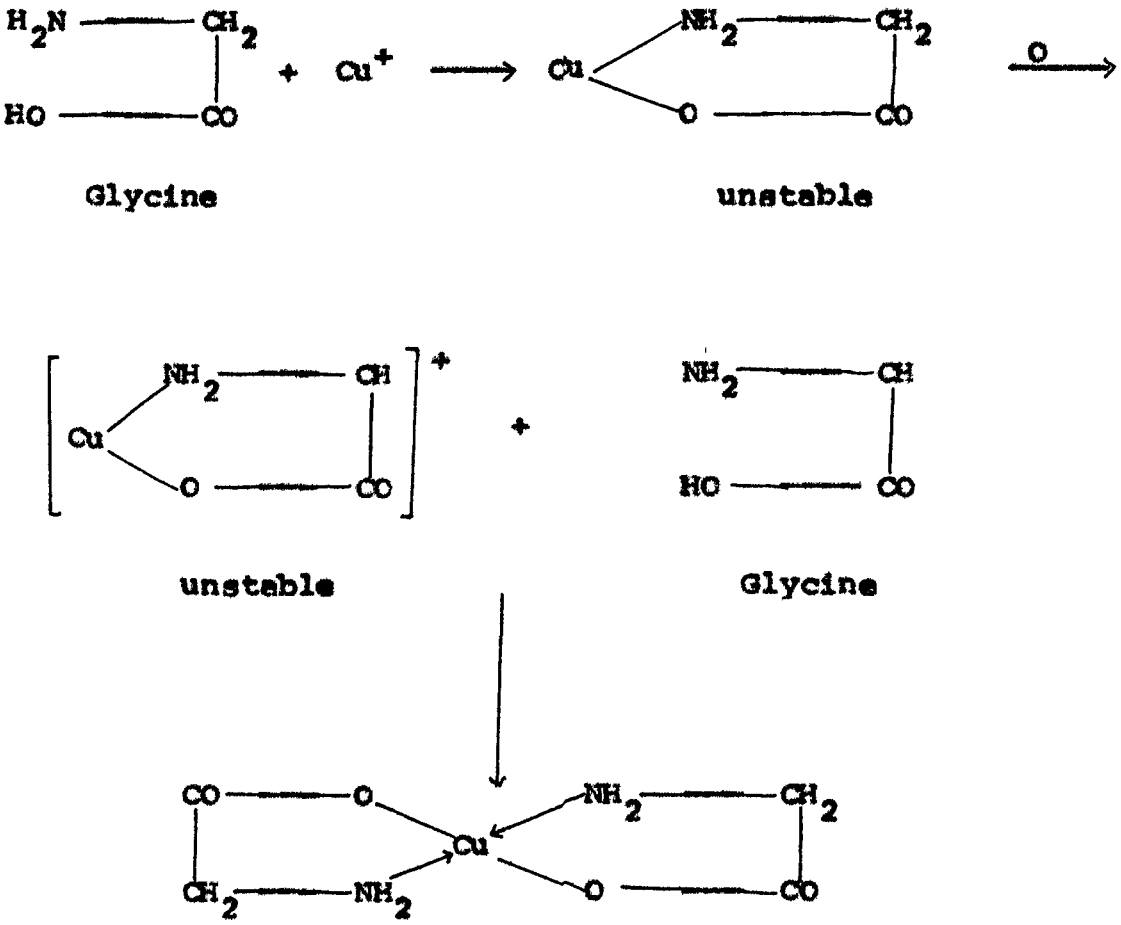
Solubility data for L-proline - Cu_2I_2 complex. Temp.25°C

Conc.of Cu_2I_2/10ml without L-proline x 10^{-5}M	Conc.of Cu_2I_2/10ml with L-proline x 10^{-5}M	Difference in Conc. of Cu_2I_2/10 ml x 10^{-5}M	Original Conc.of L-proline/ 10 ml x 10^{-5}M	Conc.of L-proline consumed/ 10 ml x 10^{-5}M	Difference in Conc.of L-proline/ 10 ml x 10^{-5}M	Ratio (Metal: Ligand)
1	2	3	4	5	6	7
14.20	16.88	2.68	7.50	2.70	4.80	1:1
8.82	12.85	4.05	10.00	4.00	6.00	1:1
6.19	10.45	4.35	12.50	4.28	8.22	1:1
2.40	6.90	4.50	15.0	4.50	10.50	1:1
1.42	6.47	5.05	17.50	5.00	12.50	1:1

RESULTS AND DISCUSSION

The solubility behaviour of copper (I) iodide in aqueous potassium iodide was studied in the presence of aminoacids such as glycine, L-proline and L-leucine. For each aminoacid system the solubility of Cu^+ was determined in two sets of solutions, the one without and the other with aminoacid. From the solubility data it appears that there was appreciable difference in Cu^+ contents of the two sets. This is an indirect evidence for complex formation in the solution containing cuprous iodide and aminoacids. The difference in the actual concentration of the aminoacid added to the copper (I) solution initially and that estimated subsequently gives the concentration of aminoacid bounded to the metal.

In tables 2A, 2B and 2C are given the concentration values of copper (I) and aminoacid in two sets of each aminoacid namely, glycine, L-leucine and L-proline, respectively. The concentration of Cu_2I_2 combined with aminoacid was determined by substracting the concentrations of Cu_2I_2 in aqueous KI without aminoacids from that of Cu_2I_2 in the same concentration of KI, but in the presence of aminoacids. Similarly, the concentration of aminoacid consumed in complex formation was determined by the difference of the concentration

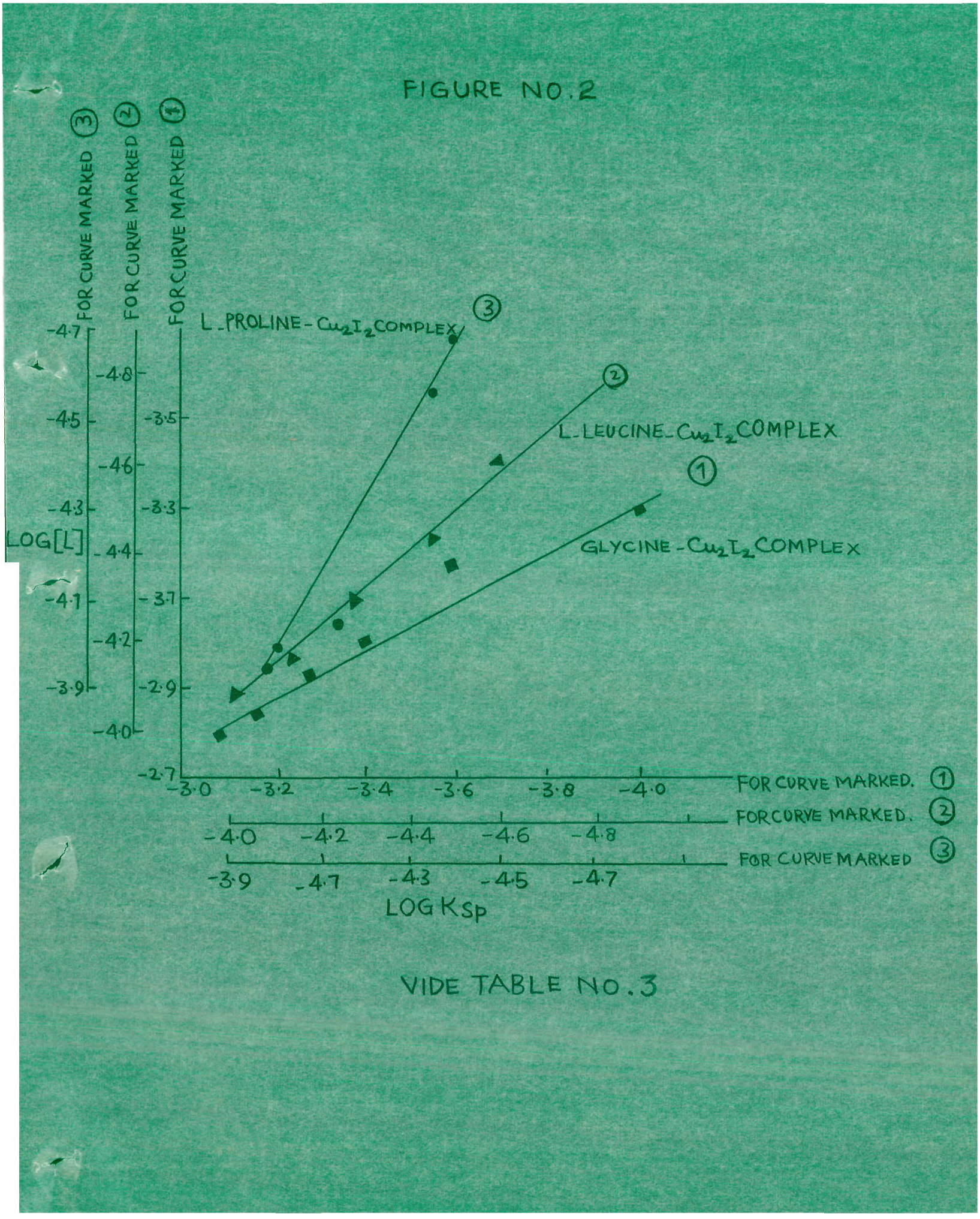


Glycine - Copper (I).

(III)

Further information regarding the behaviour of copper(I) iodide in aminoacid was obtained by seeking a relationship between Ksp, the solubility constant and the concentration of aminoacids [L] .

FIGURE NO. 2



VIDE TABLE NO. 3

TABLE No. 3

Glycine-Cu_2I_2 Complex.		L-proline-Cu_2I_2 Complex.		L-leucine-Cu_2I_2 Complex.	
log K_{sp}	log [L]	log K_{sp}	log [L]	log K_{sp}	log [L]
-4.0509	-3.3288	xxx	xxx	-4.6024	-4.5850
-3.5657	-3.2048	-4.6880	-4.3921	-4.4268	-4.4559
-3.3996	-3.0428	-4.5545	-4.3553	-4.3024	-4.2676
-3.2608	-3.9333	-4.0888	-4.1531	-4.1536	-4.2006
-3.1506	-2.8447	-3.9788	-4.0325	-4.1551	-4.1427
-3.0750	-2.7736	-3.9413	-3.9850	-4.0890	-4.0132

In table 3 are given the values of free aminoacid concentration [L] and Ksp, the solubility product of the aminoacid complex. The value of log Ksp was evaluated from $\sqrt{[M][L]^2}$ for 1:2 complex and $\sqrt{[M][L]}$ for 1:1 complex, where [M] is the original concentration of Cu^+. A linear relationship is obtained on plotting the logarithm of Ksp versus the concentration [L] of the aminoacid. From the slopes of the lines a combining ratio of 1:1 for L-leucine and L-proline, and 1:2 for glycine is indicated supporting thereby, the results of solubility measurements (Fig. No. 2).

The information regarding the complex formation between cuprous ions and aminoacid is based entirely on the analytical data obtained from solubility measurements. It could not be supported by any other physico-chemical method due to the highly

insoluble nature of cuprous iodide. However, the existing data give some evidence regarding the hitherto unknown coordinating capability of aminoacid towards cuprous ions. All attempts to isolate the complexes in solid states were unsuccessful. The inability of cuprous complexes to exist in the solid state may be explained on the basis of their lower lattice but higher solvation energies.

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C H A P T E R - III:

SUBSTITUTION REACTIONS OF SQUARE PLANAR TETRAKIS (THIOUREA) PALLADIUM (II) CHLORIDE, COMPLEX WITH SOME AMINO ACIDS.

I N T R O D C U C T I O N

The studies of the substitution reactions of square planar complexes mostly belonging to d^8 system e.g., Ni(II), Pt(II) and Pd(II) have been the subject of extensive investigations during the last one decade. The Pt(II) complexes have been synthesised in large numbers and their reactions studied in detail. However, the corresponding low spin d^8 square planar complexes of Ni(II), Pd(II), Au(III), Rh(I) and Ir(I) have been examined to a lesser extent. The recent approach to the coordination chemistry of square planar complexes mainly concerns with the kinetics and mechanism of their reactions. The main investigators in this field are Basolo, Pearson, Gray, Chatt and a few others, who enriched the field by studying the kinetics and mechanism of the substitution reactions of square planar complexes of Pt(II), Pd(II) and to a lesser extent Ni(II). The electronic structures of the square planar complexes and their substitution products have also been a field of extensive research during the last five years, specially, Gray[1,2] gave some precise and simple molecular orbital calculations regarding the bonding, and structures of these complexes. With the advent of n.m.r and e.s.r techniques, and with the substential support from electrometric techniques, like infra red, magnetic

measurements, potentiometry, polarography, spectrophotometry and conductometry, the field of substitution reactions of square planar complexes stimulated some larger interests than any other field relating to the studies of inroganic reactions.

Werner[3] was the first to give a concept of a square configuration, the other than a tetrahedral which was prevailing during the earlier years of coordination theory. He stated that α and β forms of $[Pt(NH_3)_2]Cl_2$, complex prepared long back could only be explained on the basis of a square configuration, the α-form possessing the cis and the β-form the trans configuration. However, the assignment of the structures based on some stereospecific assumptions were not found very convincing. The real break through in the syntheses of cis and trans Pt(II) complexes arrived by Chernyaev[4], who introduced the concept of the "Trans Effect" to explain many of the reactions of these complexes. According to him the negative ligands like fluoride has a greater labilising effect on a group trans to it than it does on groups in cis positions. Also this labilising effect is usually larger for a negative ligand than for a non π-bonding neutral group such as NH_3. The trans effect phenomenon was utilised by chemists[5,6,7] specially from Russia, to synthesise the desired cis and

trans isomers of Pt(II) complexes, for example, cis $Pt(NH_3)_2Cl_2$ reacts with thiourea to yield $Pt(tu)_4Cl_2$ whereas under the same conditions the trans isomer gives $Pt(tu)_2Cl_2$. On the basis of extensive studies on the trans directing influence of various ligands, the approximate order of decreasing trans effect was found to be: $CO, CN^-, C_2H_4 > PR_3H^- > CH_3^-, SC(NH_2)_2 > C_6H_5^-, NO_2^-, I^-, SCN^- > Br^-, Cl^- > Py, NH_3, OH^-, H_2O$. Kinetically, the extent of the effect can be estimated by the fact that a good trans labilising agent is 10^6 or more in rate than that of the ligand, low in the trans effect series.[8]

A very large number of reactions of platinum complexes of the type cis and trans Pt A_2L x with Y to yeld Pt A_2LY have been studied, and the cis substrates yield cis products and trans give trans.[9] The fact that there is complete retention of the configuration as such indicated by the mechanism having a high degree of stereospecificity. This can be achieved by a nucleophilic attack through a trigonal bipyramidal structure. There are numerous evidences of the tendencies of d^8 low spin tetra coordinate system to add additional ligands and forming five, and/or six coordinated complexes. Compounds of the type, $M(diers)_2x_2$ where M is Ni(II), Pd(II), or Pt(II) are univalent electrolytes

in nitrobenzene[10] and the compounds, Ir $(P\text{-}Ph_3)_3(C{=}O)_2Cl$[11] and $Rh(P\text{-}Ph_3)_3COH$[12] have been isolated. These complexes together with 5-coordinate Pt(II) anions, $Pt(SnCl_3)_5^{3-}$, $Pt\,H\,(SnCl_3)_4^{3-}$ and $Pt(Pet_3)_2H\,(SnCl_3)_2^{1-}$ found to have trigonal bipyramidal structures.[13] It is found that these ligands are strongly π-bonding in nature and are, therefore, good trans activators and this stabilises the five coordinated transition states.[14] Basolo and his associates,[15] with the help of a variety of widest range data collected from the reactions of trans $Pt(Pet_3)_2\,LCl$ with pyridine to yield trans $Pt(Pet_3)_2\,L\,Py^{1-}$, where $L = P(C_2H_5)_3H^-$, CH_3^-, $P\text{-}ClC_6H_4^{1-}$ etc., reported that the total range in reactivities covers a wide span of 10^5 with $L{=}H^-$ and $P(et)_3$, the fastest, and $L{=}Cl^-$, the slowest. The effect of leaving group in a system like $Pt(dien)\,x^+ + Py \longrightarrow Pt(dien)\,Py^{2+} + x^{-1}$ has been studied by Basolo, Gray and Pearson.[16] In this complex, the three other coordination positions are kept constant by using the inert dien ligand, and the entering ligand is always pyridine. The only variable is x^-. From the $K_{obsd.}$ values the decreasing rate for changes in x^- follow the order: $NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2 > CN^-$. The spread in rates from NO_3^- to CN^- is approximately 10^6, thus showing that the leaving group has a substantial effect on the rate of reaction and considerable bond breaking is involved in the formation

of 5-coordinated transition states. Another important factor, which influenced the rate of reactions, is the steric effect. If a bimolecular displacement is involved, the increased steric hinderence causes a decrease in the rate, whereas steric acceleration is generally observed for a dissociation process.

A comparison of the rate of reaction of $Pt(et_4\ dien)Cl^+$ with that of analogous and unhindered $Pt(dien)Cl^+$ shows that the hindered systems react more slowly by several orders of magnitude.[17] The most interesting example to depict the above picture is the comparison of the reactions of the five coordinated complexes, $Pt(TAS)x^+$ and $Pt(QAS)x^+$, the reactions of the former are approximately 10^4 times faster than the reactions of the more sterically crowded complex, $Pt(QAS)x^+$.

The kinetic data regarding the substitution reactions of Pd(II) complexes are rather limited, but they are essentially of square planar substitution type. The Pd(II) systems are more reactive than corresponding Pt(II) systems. This is due to much weaker strength of Pd-X bond in the complexes of the type $Pd\ LX^+$. For example, a comparison of the rate of reactions of Pd(II) and Pt(II) complexes of the type $M(dien)X^+$ with pyridine indicates that Pd(II) systems are approximately 10^5 times more reactive.[18] Another

interesting example of the substitution reactions of square planar Pd(II), Pt(II) and Ni(II) complexes (containing unidentate ligands) is their reaction with pyridine,[15]

trans-$M(Pet_3)_2$(-tolyl)Cl+Py ⟶ trans-$M(Pet_3)_2$(0-tolyl)Py^++Cl^-.

The rate of reaction increases with increase in concentration and follows the typical two terms rate law. The values of rate constants for solvent path, K, for the three metal ions indicate that the rates of reactions decreased in the order:

Relative rates:	Ni(II)	Pd(II)	Pt(II)
	$5x10^6$	$1x10^6$	1.0

The comparative values of the rates of reactions indicate an increase in stability of the complex with decrease in the rates of reactions.

From a brief survey of the substitution reactions of square planar Pt(II) and Pd(II) complexes described above, it appears that the studies are largely concentrated on amine complexes and the effect of entering groups have been correlated with the trans directing properties, and nucleophilic reactivities of these ligands. During the course of studies on the interaction of aminoacids with square planar complex, $Pd(tu)_4Cl_2$, it was found that the kinetics of the substitution reactions could be studied

and possible mechanism may be put forward. The role of aminoacids as entering ligand has not yet been investigated in Pt(II) and Pd(II) complexes, and the present study concerns with the substitution reactions of $Pd(tu)_4Cl_2$ with a variety of aminoacids. The results of investigations concerning with the reactions of tetrakis (thiourea) palladium(II) chloride with some aminoacids are described in the proceeding pages.

EXPERIMENTAL

Chemicals:

The aminoacids, glycine, DL-α-alanine, L-proline, L-asparagine, DL-serine, threonine and DL-valine (B.D.H. biologically pure products) were used. Palladium(II) chloride (Jhonson and Matthy, London) and thiourea(B.D.H) were employed for preparing the complex, $Pd(tu)_4Cl_2$. The solutions were prepared in doubly distilled, air free water.

Preparation of complex, tetrakis(thiourea) palladium(II) chloride:

About 50 ml solution of 1% $PdCl_2$ in HCl was taken in a flask and about 5 gms of solid thiourea was added to it, the resulting mixture was heated over a water bath till all

the thiourea was dissolved. Any insoluble residue left was filtered out, the filtrate diluted by adding 50 ml of water and evaporated to one half of its volume. The resulting solution was kept for crystallisation and after about 72 hours red crystals of the complex appeared, which were then separated from the main liquor, washed with acetone and dried in a desiccator over CaO. Analytical data: Calculated for $C_4H_{16}N_8S_4$ $PdCl_2$: C-9.9, H-3.3, N-23.1, S-26.6, Found:- C-10.10, H-3.3, N-23.2, S-26.5.

Apparatus: Spectrophotometric measurements were carried out by using a Bausch & Lomb spectronic '20' spectrophotometer and 1 cm cuvettes. The selection of wave-length was made by first plotting the spectrum of complex, $Pd(tu)_4Cl_2$ in the region 350 to 625 mμ. The λmax. of the complex was observed at 360 mμ. With aminoacids the selection of wave length was made at 575 mμ where thiourea complex and aminoacid complex have vast difference in absorbencies, the latter having stronger absorbance. The absorbencies of the aminoacid complexes $(O.D)_\infty$ were obtained by keeping the mixture over night and measuring the absorption until reasonably constant values were obtained. All the measurements were carried out at constant temperature by dipping the containers of these solutions in a thermostat(type N.B.E, Germany) with a sensitivity of $\pm$ 0.5°C.

The first order rate[8] was determined by plotting $\log \frac{(O.D.)_{\infty} - (O.D.)_o}{(O.D.)_{\infty} - (O.D.)_t}$ versus time ti and the rate constant $K_{obsd.}$ is given by the expression.

$$K_{obsd.} = \frac{2.303}{t} \log \frac{(O.D.)_{\infty} - (O.D.)_o}{(O.D.)_{\infty} - (O.D.)_t}$$

where $K_{obsd.}$ is the observed first order constant, $(O.D.)_{\infty}$ is the maximum absorbance, $(O.D.)_t$ is the absorbance value at time t; and $(O.D.)_o$, is the initial absorbance value. Values of rate constant were calculated from 2.303 times the slope of the linear rate plots (Fig. Nos. 1 to 7).

TABLE No. 1

Calculated values of log $\frac{(O.D.)_\infty - (O.D.)_o}{(O.D.)_\infty - (O.D.)_t}$ for glycine $-Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C.

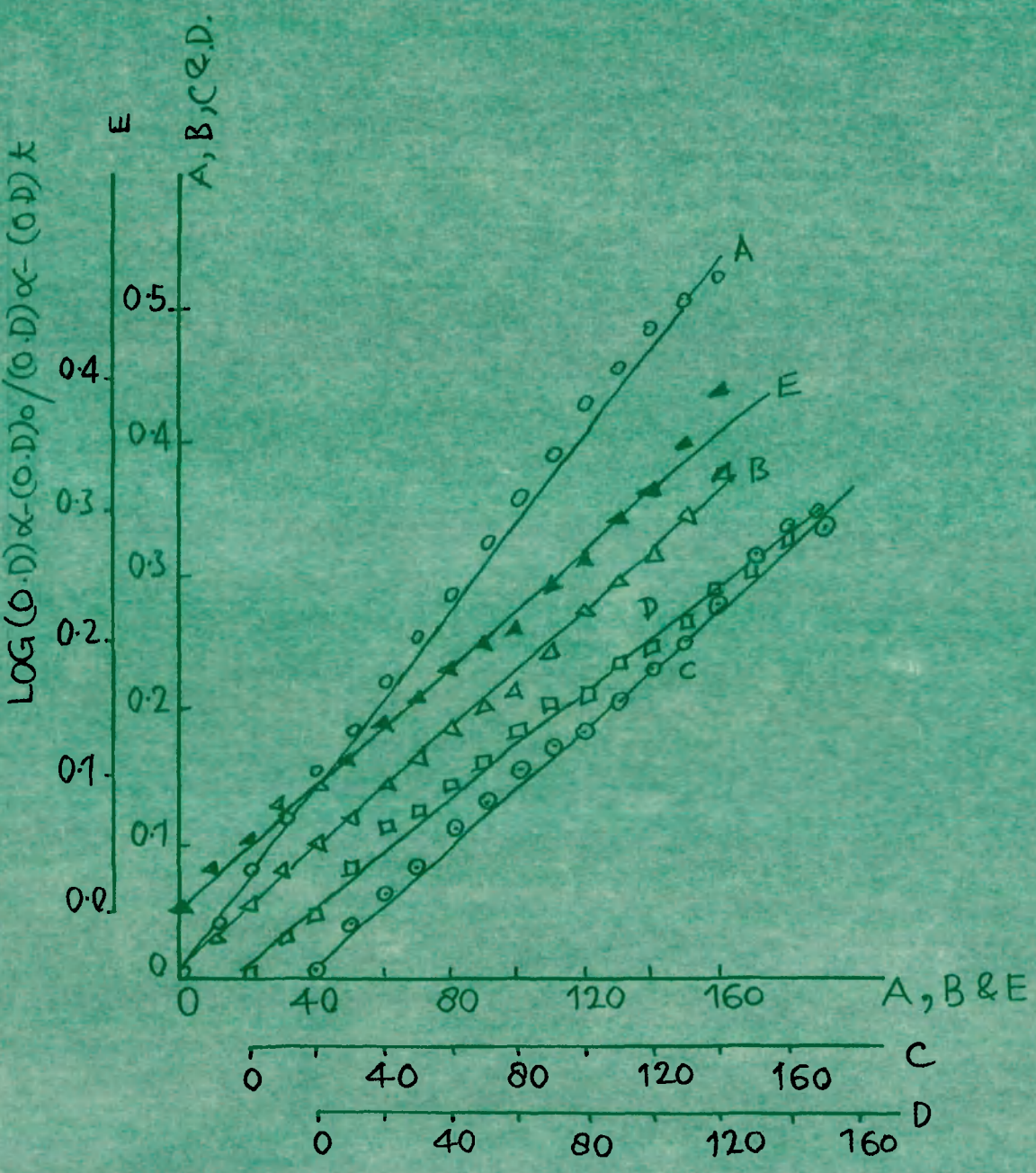
$$\log \frac{(O.D.)_\infty - (O.D.)_o}{(O.D.)_\infty - (O.D.)_t}$$

Time in minutes	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.040	0.028	0.026	0.042	0.038
20	0.080	0.057	0.038	0.066	0.055
30	0.123	0.078	0.088	0.088	0.074
40	0.157	0.099	0.113	0.112	0.096
50	0.186	0.119	0.126	0.131	0.119
60	0.225	0.142	0.148	0.152	0.141
70	0.259	0.160	0.167	0.172	0.164
80	0.286	0.181	0.187	0.189	0.176
90	0.326	0.200	0.203	0.206	0.195
100	0.358	0.219	0.214	0.2369	0.214
110	0.393	0.240	0.231	0.256	0.241
120	0.431	0.272	0.242	0.276	0.266
130	0.458	0.295	0.259	0.290	0.393

(Contd.)

FIGURE NO. 1

PLOTS OF $\log \frac{(O.D.)_\infty - (O.D)_0}{(O.D)_\infty - (O.D)_t}$ Vs. t AT VARIOUS CONCENTRATIONS OF GLYCINE



VIDE TABLE NO. 1

Time in minutes	A	B	C	D	E
140	0.487	0.319	0.285	0.312	0.317
150	0.502	0.345	0.304	0.327	0.352
160	0.524	0.372	0.325	0.343	0.390

Conc. of $Pd(tu)_4Cl_2$ = 1 x 10^{-3}M, Ionic strength = 0.10

(A) $1x10^{-1}$M glycine, $(O.D.)_{\alpha}$ = 0.95, $(OD.)_{o}$ = 0.06

(B) $5x10^{-2}$M " $(O.D.)_{\alpha}$ = 0.80, $(O.D.)_{o}$ = 0.07

(C) $3.3x10^{-2}$M " $(O.D.)_{\alpha}$ = 0.70, $(O.D.)_{o}$ = 0.045

(D) $2.5x10^{-2}$M " $(O.D.)_{\alpha}$ = 0.65, $(O.D.)_{o}$ = 0.055

(E) $2.0x10^{-2}$M " $(O.D.)_{\alpha}$ = 0.60, $(O.D.)_{o}$ = 0.06

(Vide Fig. No. 1)

TABLE No. 2

Calculated values of log $\frac{(O.D.)_{\alpha} - (O.D.)_{o}}{(O.D.)_{\alpha} - (O.D.)_{t}}$ for DL-α-alanine -$Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C.

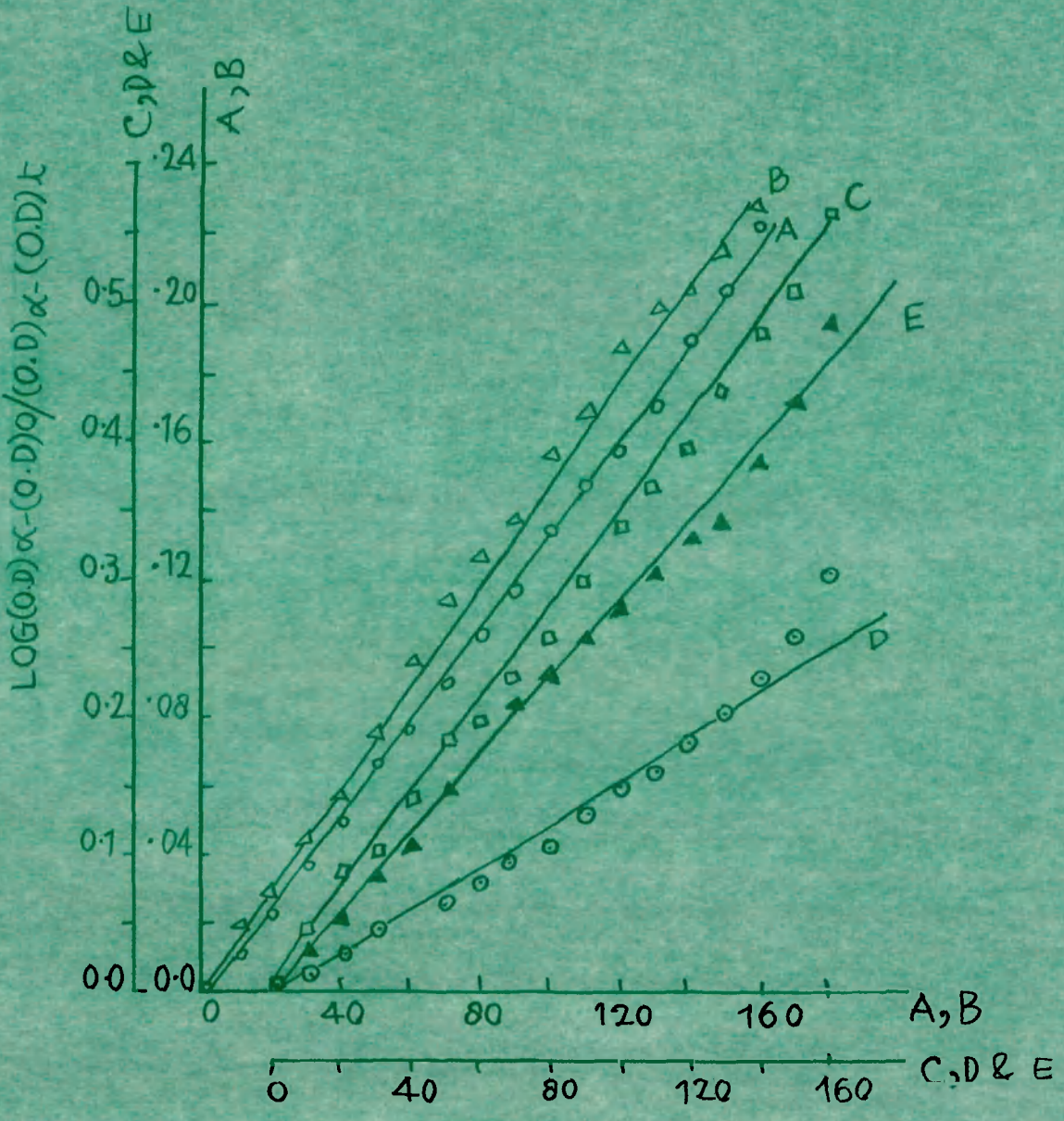
$$\log \frac{(O.D.)_{\alpha} - (O.D.)_{o}}{(O.D.)_{\alpha} - (O.D.)_{t}}$$

Time in minute.	A	B	C.	D	E
0.	0.00	0.00	0.00	0.00	0.00
10	0.013	0.019	0.019	0.013	0.028
20	0.022	0.029	0.034	0.028	0.053
30	0.037	0.043	0.040	0.042	0.084
40	0.049	0.057	0.055	0.049	0.107
50	0.065	0.076	0.072	0.061	0.149
60	0.077	0.094	0.078	0.076	0.204
70	0.089	0.112	0.091	0.093	0.218
80	0.102	0.125	0.105	0.109	0.234
90	0.114	0.138	0.119	0.126	0.258
100	0.133	0.155	0.134	0.145	0.275
110	0.145	0.168	0.145	0.164	0.301
120	0.154	0.186	0.157	0.183	0.328
130	0.168	0.198	0.174	0.204	0.339

(Contd.)

FIGURE NO. 2

PLOTS OF $\log\frac{(O.D)\alpha-(O.D)o}{(O.D)\alpha-(O.D)t}$ VS. t AT VARIOUS CONCENTRATIONS OF DL-α-ALANINE



TIME IN MINUTES

VIDE TABLE NO. 2

Time in minute.	A	B	C	D	E
140	0.183	0.202	0.190	0.226	0.380
150	0.208	0.213	0.207	0.260	0.426
160	0.222	0.225	0.225	0.301	0.487

Conc. of $Pd(tu)_4Cl_2$ = $1x10^{-3}$M, Ionic strength = 0.10

(A) $1x10^{-1}$M DL-α-Alanine, $(O.D.)_\alpha$ = 1.4, $(O.D.)_o$ = 0.06

(B) $5x10^{-2}$M " " $(O.D.)_\alpha$ = 0.95, $(O.D.)_o$ = 0.05

(C) $3.3x10^{-2}$M " " $(O.D.)_\alpha$ = 0.85, $(O.D.)_o$ = 0.06

(D) $2.5x10^{-2}$M " " $(O.D.)_\alpha$ = 0.70, $(O.D.)_o$ = 0.045

(E) $2.0x10^{-2}$M " " $(O.D.)_\alpha$ = 0.52, $(O.D.)_o$ = 0.04

(Vide Fig. No. 2)

TABLE No.3

Calculated values of log $\frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$ for L-proline -$Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C.

$$\log \frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$$

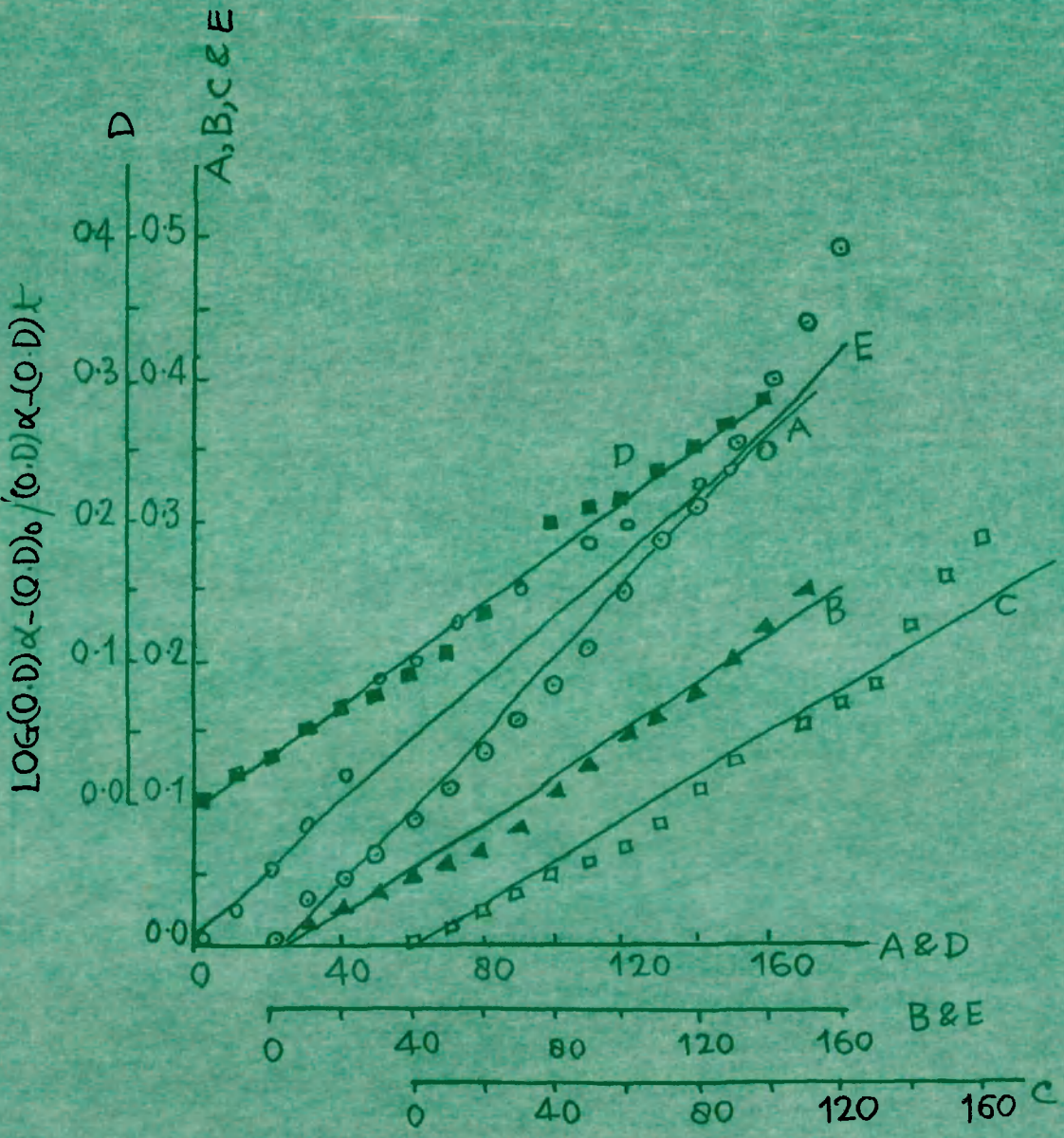
Time in minutes	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.020	0.018	0.010	0.020	0.026
20	0.057	0.028	0.021	0.034	0.045
30	0.088	0.037	0.032	0.048	0.065
40	0.122	0.043	0.043	0.063	0.086
50	0.179	0.053	0.055	0.071	0.107
60	0.200	0.068	0.066	0.087	0.130
70	0.222	0.079	0.082	0.103	0.156
80	0.244	0.101	0.118	0.138	0.180
90	0.256	0.125	0.132	0.156	0.207
100	xx	0.149	0.138	0.196	0.252
110	0.2814	0.162	0.153	0.206	0.284
120	0.294	0.176	0.168	0.217	0.318

(Contd.)

FIGURE NO. 3

PLOTS OF LOG $\frac{(O.D)\alpha - (O.D)_0}{(O.D)\alpha - (O.D)t}$ Vs. t AT VARIOUS CONCENTRATIONS.

OF L-PROLINE



TIME IN MINUTES

VIDE TABLE NO. 3

Time in minutes	A	B	C	D	E
130	0.307	0.204	0.183	0.239	0.356
140	0.321	0.226	0.225	0.251	0.398
150	0.335	0.249	0.261	0.263	0.444
160	0.348	xx	0.280	0.288	0.495

Conc. of $Pd(tu)_4Cl_2$ = $1x10^{-3}$M, Ionic strength = 0.10

(A) $1x10^{-1}$M L-Proline, $(O.D.)_{\infty}$ = 0.68, $(O.D.)_o$ = 0.03

(B) $5x10^{-2}$M L-Proline, $(O.D.)_{\infty}$ = 0.52, $(O.D.)_o$ = 0.04

(C) $3.3x10^{-2}$M L-Proline, $(O.D.)_{\infty}$ = 0.45, $(O.D.)_o$ = 0.03

(D) $2.5x10^{-2}$M L-Proline, $(O.D.)_{\infty}$ = 0.36, $(O.D.)_o$ = 0.03

(E) $2.0x10^{-2}$M L-Proline, $(O.D.)_{\infty}$ = 0.29, $(O.D.)_o$ = 0.04

(Vide Fig. No 3)

TABLE No. 4

Calculated values of log $\frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$ of DL-serine -$Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C

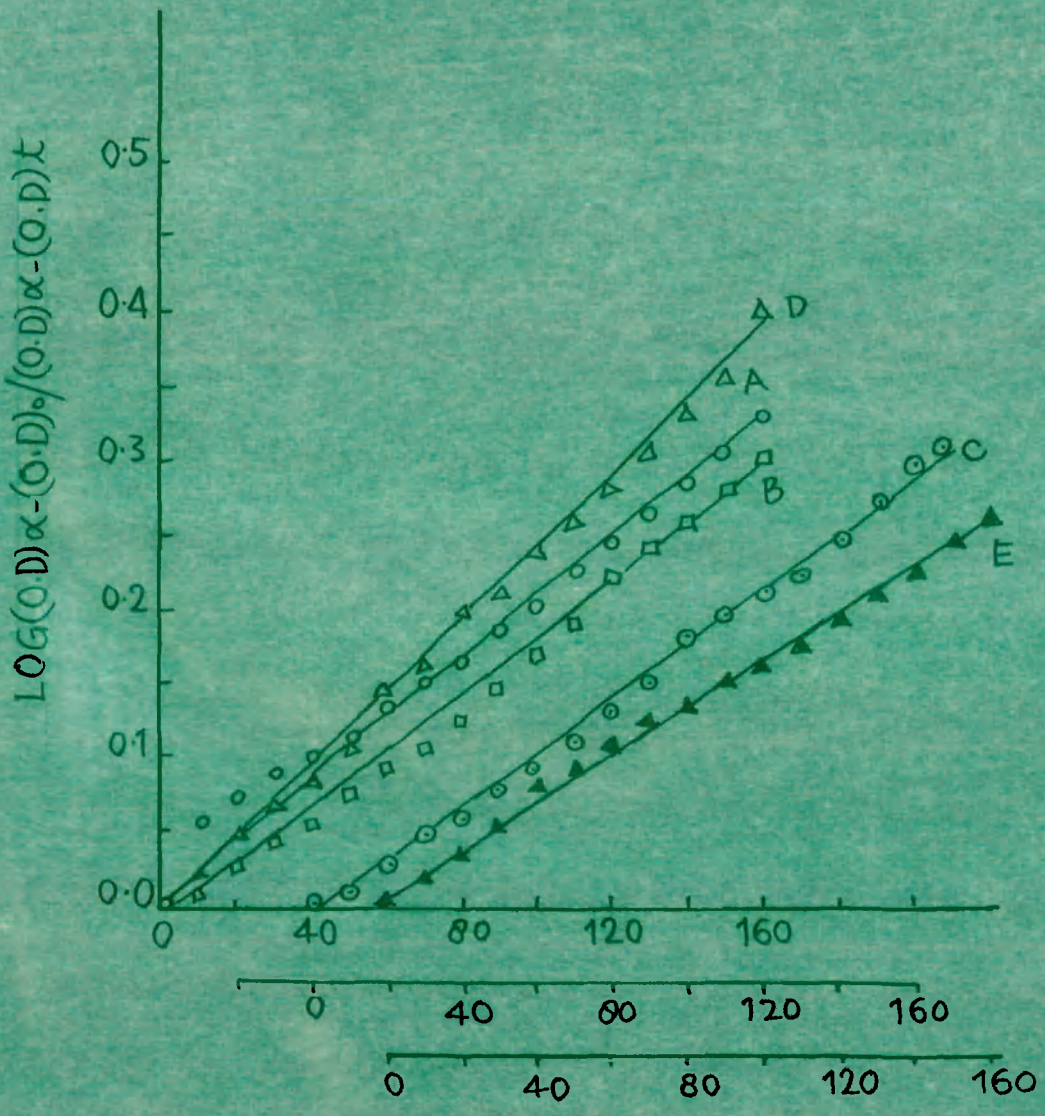
$$\log \frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$$

Time in minute.	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.062	0.117	0.016	0.024	0.021
20	0.079	0.028	0.033	0.050	0.035
30	0.089	0.043	0.051	0.071	0.057
40	0.104	0.058	0.068	0.085	0.082
50	0.119	0.075	0.083	0.115	0.090
60	0.135	0.092	0.097	0.147	0.116
70	0.151	0.109	0.114	0.164	0.125
80	0.167	0.127	0.134	0.209	0.134
90	0.185	0.146	0.156	0.219	0.153
100	0.203	0.171	0.180	0.240	0.163
110	0.242	0.225	0.211	0.283	0.193

(Contd.)

FIGURE NO. 4

PLOTS OF LOG $(O.D)_\infty - (O.D)_0 / (O.D)_\infty - (O.D)_t$ Vs. t AT VARIOUS CONCENTRATIONS OF DL-SERINE



VIDE TABLE NO. 4

Time in minutes	A	B	C	D	E
120	0.242	0.225	0.211	0.293	0.193
130	0.262	0.243	0.231	0.307	0.215
140	0.285	0.267	0.245	0.332	0.226
150	0.307	0.287	0.274	0.358	0.249
160	0.331	0.301	0.297	0.416	0.262

Conc. of $Pd(tu)_4Cl_2$ = $1x10^{-3}M$, Ionic strength = 0.10

(A) $1x10^{-1}M$ DL-serine, $(O.D.)_{\alpha}$ = 0.75 $(O.D.)_o$=0.08

(B) $5x10^{-2}M$ DL-serine, $(O.D.)_{\alpha}$ = 0.70 $(O.D.)_o$=0.07

(C) $3.3x10^{-2}M$ DL-Serine, $(O.D.)_{\alpha}$ = 0.62 $(O.D.)_o$=0.075

(D) $2.5x10^{-2}M$ DL-serine, $(O.D.)_{\alpha}$ = 0.43 $(O.D.)_o$=0.065

(E) $2.0x10^{-2}M$ DL-serine, $(O.D.)_{\alpha}$ = 0.38 $(O.D.)_o$=0.06

(Vide Fig. No. 4)

TABLE No. 5

Calculated values of log $\frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$ for L-asparagine -$Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C

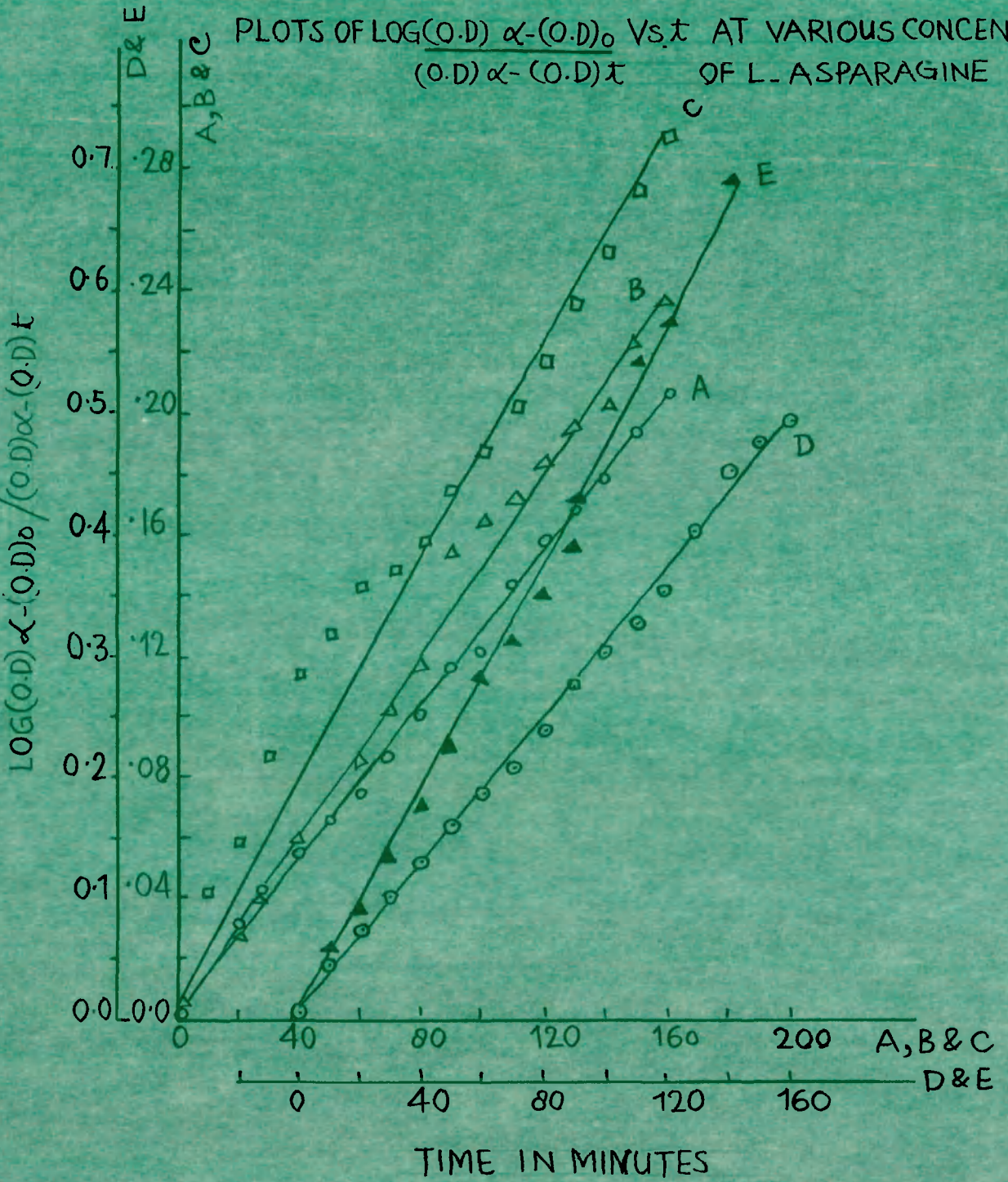
$$\log \frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$$

Time in minutes	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.018	0.018	0.042	0.049	0.051
20	0.032	0.034	0.059	0.076	0.089
30	0.043	0.042	0.089	0.108	0.130
40	0.055	0.058	0.115	0.125	0.176
50	0.066	0.061	0.128	0.169	0.227
60	0.074	0.084	0.142	0.189	0.285
70	0.086	0.102	0.149	0.209	0.317
80	0.103	0.116	0.156	0.242	0.352
90	0.117	0.151	0.171	0.276	0.390
100	0.121	0.162	0.186	0.301	0.452
110	0.144	0.172	0.202	0.327	0.556
120	0.159	0.183	0.218	0.355	0.586

(Contd.)

FIGURE NO. 5

PLOTS OF LOG $\frac{(O.D)\infty - (O.D)_0}{(O.D)\infty - (O.D)t}$ Vs. t AT VARIOUS CONCENTRATIONS OF L-ASPARAGINE



VIDE TABLE NO. 5

Time in minutes	A	B	C	D	E
130	0.169	0.195	0.235	0.401	0.691
140	0.179	0.206	0.253	0.452	0.732
150	0.195	0.218	0.272	0.471	0.778
160	0.206	0.230	0.291	0.490	0.795

Conc. of $-Pd(tu)_4Cl_2$ = $1x10^{-3}M$, Ionic strength = 0.10

(A) $1x10^{-1}M$ L-asparagine, $(O.D.)_\infty$ = 0.70, $(O.D.)_o$ = 0.065

(B) $5x10^{-2}M$ L-asparagine, $(O.D.)_\infty$ = 0.65, $(O.D.)_o$ = 0.055

(C) $3.3x10^{-2}M$ L-asparagine, $(O.D.)_\infty$ = 0.48, $(O.D.)_o$ = 0.05

(D) $2.5x10^{-2}M$ L-asparagine, $(O.D.)_\infty$ = 0.39, $(O.D.)_o$ = 0.05

(E) $2.0x10^{-2}M$ L-asparagine, $(O.D.)_\infty$ = 0.32, $(O.D.)_o$ = 0.05

(Vide Fig. No. 5)

TABLE No. 6

Calculated values of log $\frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$ for DL-threonine-$Pd(tu)_4Cl_2$ system at various concentrations. Temp. = 35°C

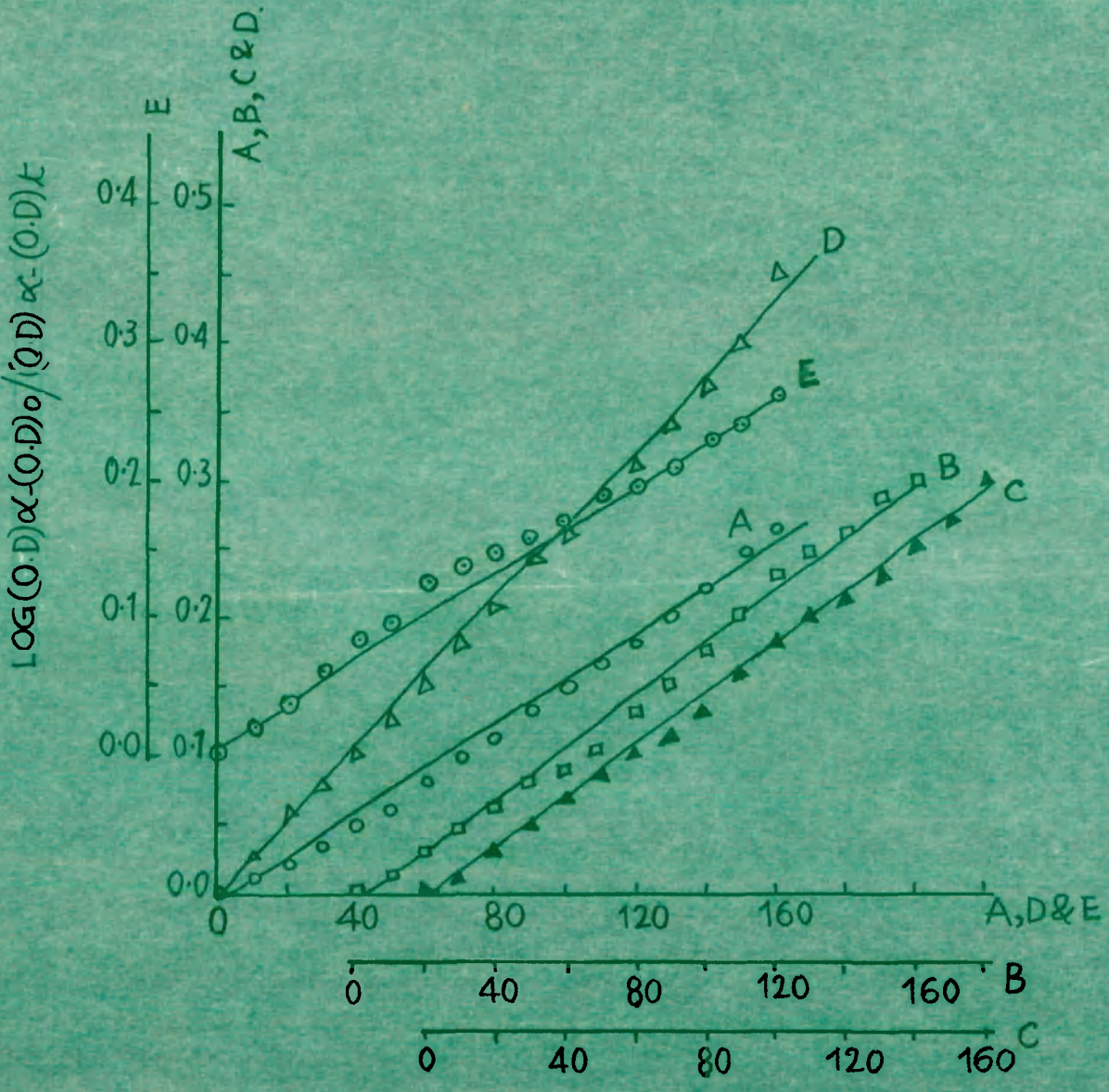
$$\log \frac{(O.D.)_{\infty} - (O.D.)_{o}}{(O.D.)_{\infty} - (O.D.)_{t}}$$

Time in minutes	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.013	0.018	0.016	0.026	0.022
20	0.020	0.029	0.033	0.064	0.038
30	0.034	0.045	0.052	0.076	0.063
40	0.049	0.062	0.070	0.102	0.089
50	0.064	0.078	0.085	0.125	0.098
60	0.080	0.087	0.100	0.153	0.127
70	0.097	0.105	0.115	0.179	0.137
80	0.114	0.133	0.137	0.212	0.147
90	0.132	0.153	0.160	0.242	0.158
100	0.150	0.179	0.184	0.264	0.168
110	0.169	0.202	0.203	0.288	0.179
120	0.189	0.237	0.216	0.314	0.191

(Contd.)

FIGURE NO. 6

PLOTS OF LOG$(O.D)_{\infty}-(O.D)_0$ Vs. t AT VARIOUS CONCENTRATIONS
$(O.D)_{\infty}-(O.D)_t$
OF DL-THREONINE



VIDE TABLE NO. 6

Time in minutes	A	B	C	D	E
130	0.200	0.250	0.237	0.341	0.214
140	0.222	0.269	0.254	0.370	0.226
150	0.247	0.290	0.274	0.401	0.239
160	0.268	0.304	0.305	0.452	0.265

Conc. of $Pd(tu)_4Cl_2$ complex = $1x10^{-3}$M, Ionic strength 0.1

(A) $1x10^{-1}$M DL-threonine, $(O.D.)_{\alpha}$ = 0.73 $(O.D.)_{o}$ = 0.08

(B) $5x10^{-2}$M DL-threonine, $(O.D.)_{\alpha}$ = 0.68 $(O.D.)_{o}$ = 0.76

(C) $3.3x10^{-2}$M DL-threonine, $(O.D.)_{\alpha}$ = 0.605 $(O.D.)_{o}$ = 0.07

(D) $2.5x10^{-2}$M DL-threonine, $(O.D.)_{\alpha}$ = 0.40 $(O.D.)_{o}$ = 0.06

(E) $2.0x10^{-2}$M DL-threonine, $(O.D.)_{\alpha}$ = 0.35 $(O.D.)_{o}$ = 0.05

(Vide Fig. No. 6)

TABLE No. 7

Calculated values of log $\frac{(O.D.) - (O.D.)_o}{(O.D.) - (O.D.)_t}$ for DL-Valine -$Pd(tu)_4Cl_2$ system at various concentrations. Temp. 35°C

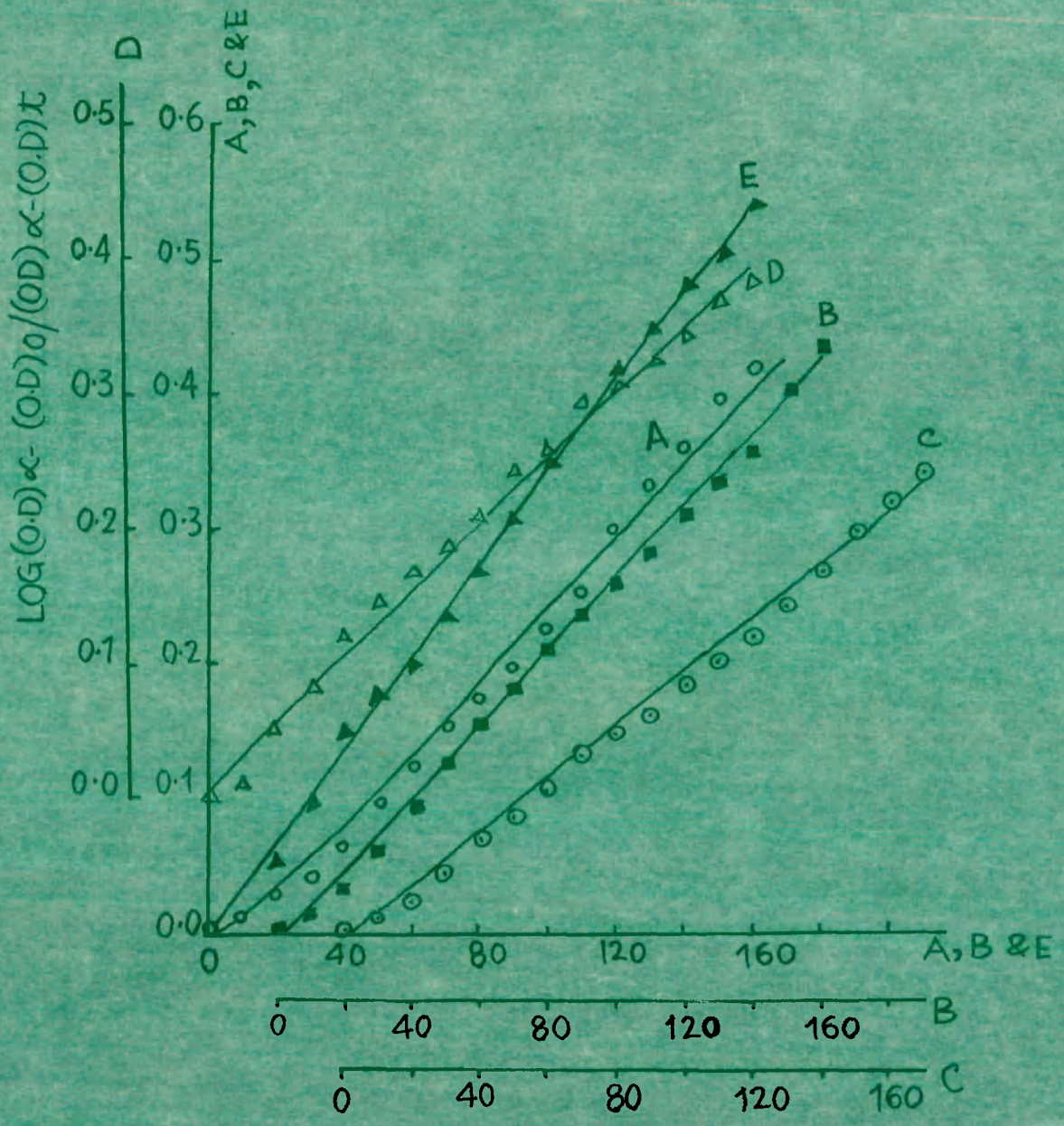
$$\log \frac{(O.D.) - (O.D.)_o}{(O.D.) - (O.D.)_t}$$

Time in minutes	A	B	C	D	E
0	0.00	0.00	0.00	0.00	0.00
10	0.010	0.012	0.014	0.017	0.016
20	0.027	0.037	0.045	0.054	0.056
30	0.041	0.064	0.071	0.084	0.094
40	0.067	0.094	0.088	0.122	0.150
50	0.094	0.125	0.106	0.145	0.173
60	0.123	0.158	0.134	0.169	0.197
70	0.154	0.185	0.149	0.189	0.232
80	0.170	0.214	0.165	0.216	0.270
90	0.196	0.239	0.187	0.244	0.312
100	0.224	0.261	0.204	0.268	0.357
110	0.253	0.289	0.222	0.293	0.395
120	0.306	0.313	0.246	0.309	0.422

(Contd.)

FIGURE NO. 7

PLOTS OF $\log \frac{(O.D)\alpha - (O.D)_0}{(O.D)\alpha - (O.D)t}$ VS. t AT VARIOUS CONCENTRATIONS. OF DL-VALINE



TIME IN MINUTES

VIDE TABLE NO. 7

Time in minutes	A	B	C	D	E
130	0.336	0.338	0.273	0.327	0.451
140	0.366	0.365	0.301	0.346	0.482
150	0.395	0.410	0.323	0.365	0.505
160	0.424	0.442	0.346	0.385	0.543

Conc. of $Pd(tu)_4Cl_2$ = $1x10^{-3}$M, Ionic strength = 0.10

(A) $1x10^{-1}$M DL-valine, $(O.D.)_\alpha$ = 0.85, $(O.D.)_o$ = 0.08

(B) $5x10^{-2}$M DL-valine, $(O.D.)_\alpha$ = 0.80, $(O.D.)_o$ = 0.08

(C) $3.3x10^{-2}$M DL-valine, $(O.D.)_\alpha$ = 0.68, $(O.D.)_o$ = 0.08

(D) $2.5x10^{-2}$M DL-valine, $(O.D.)_\alpha$ = 0.58, $(O.D.)_o$ = 0.07

(E) $2.0x10^{-2}$M DL-valine, $(O.D.)_\alpha$ = 0.48, $(O.D.)_o$ = 0.48

(Vide Fig. No. 7)

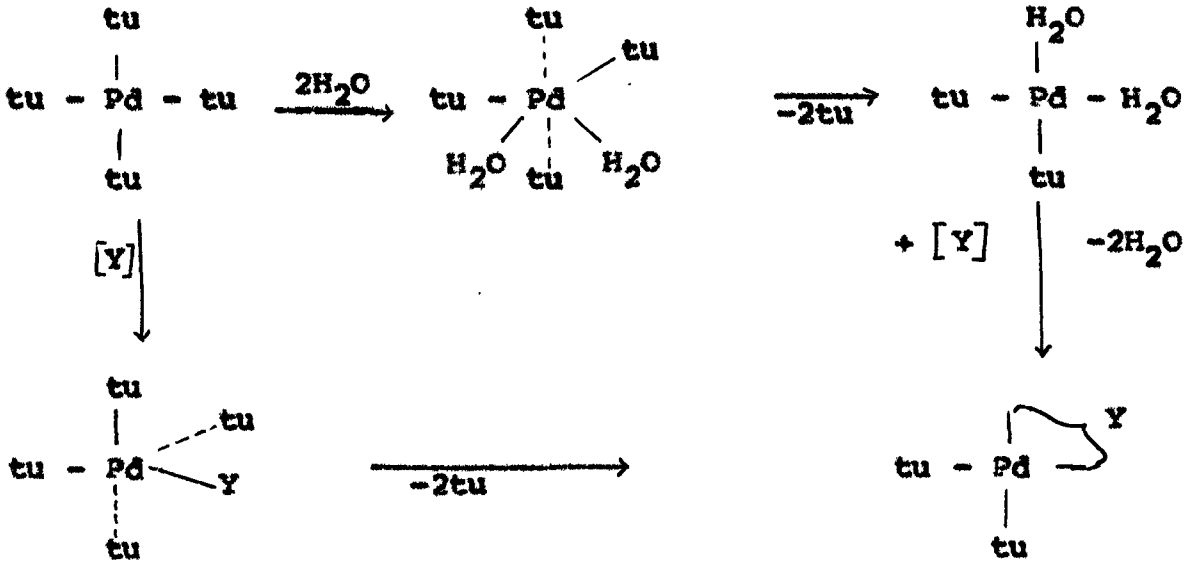
RESULTS AND DISCUSSION

The kinetics of substitution reactions of square planar tetra kis (thiourea) palladium(II) chloride, $Pd(tu)_4Cl_2$ have been studied by spectrophotometric measurements taking advantage of the fact that intense colour is developed on the addition of aminoacid in $Pd(tu)_4Cl_2$ solution, and the absorption of the latter is insignificant in comparison to absorption of the complex solution containing aminoacid at a selected wave length, 575 mμ.

In general, the kinetic data on the substitution reactions of square planar complex can be represented in terms of a bimolecular displacement mechanism following a two term rate law[1]

Rate = $K_1 [Pd(tu)_4Cl_2] + K_2 [Pd(tu)_4Cl_2] [Y]$ for the general reaction, $[Pd(tu)_4]^{++} + [Y] \rightarrow [Pd(tu)_2Y]^{+} + 2tu$, where [Y] is the aminoacid group and K_1 and K_2 are the first and second order rates, respectively. The experimental first order rate constant $K_{obsd.}$ is related to K_1 and K_2 by the reaction $K_{obsd.} = K_1 + K_2 [Y.]$ Following Basolo, the rate constant K_1 represents the slow displacements of thiourea molecules by the solvent (H_2O) which is then readily displaced by the aminoacid. A direct

nucleophilic displacement of thiourea by aminoacid is responsible for K_2. The path mechanism for the substitution by aminoacid [Y] in such a system may be represented by the following scheme.



Applying the two term rate law, the substituttion reactions of Pd(II), the plots of $K_{obsd.}$ versus [Y] for various aminoacids indicate a linear relationship in case of glycine, L-asparagine, L-proline, DL-serine and DL-α-alanine(Fig.No.8 for glycine only), however, no such relationship exists in DL-valine and threonine. The reaction with β-alanine is very fast and equilibrium is attained almost immediately, hence the value of $K_{obsd.}$ could not be determined. The sulphur containing aminoacids, methionine and taurine do not show any reactivity.

The values of rate constants $K_{obsd.}$, K_1 and K_2 for the reactions of square planar $Pd(tu)_4Cl_2$ with various aminoacids are given in the table (No.8) at constant ionic strength of 0.10 and a temperature of 35°C. The pH of the reaction mixture was maintained at about 6.5.

T A B L E No.8

Rates of reaction of square planar $Pd(tu)_4Cl_2$ complex with various aminoacids in aqueous solutions at 35°C, pH 6.5. Conc. of the complex, $Pd(tu)_4Cl_2$ = $1x10^{-3}$M, ionic strength 0.10

Aminoacid concentration	$K_{obsd.}x10^{-3}$/min.	K_1x10^{-3}/min.	K_2/mole min.
Glycine(10^{-2}M)			
10.0	8.625		
5.0	5.29		
3.3	5.02	4.10	$5.76x10^{-3}$
2.5	4.48		
2.0	5.29		

(Contd.)

Aminoacid concentration	$K_{obsd.} \times 10^{-3}$/min	$K_1 \times 10^{-3}$/min	K_2/mole.min
DL-α-Alanine (10^{-2}M)			
10.0	3.03		
5.0	3.45		
3.3	3.45	3.50	1.66×10^{-2}
2.5	3.31		
2.0	6.67		
L-Proline (10^{-2}M)			
10.0	4.10		
5.0	3.08		
3.3	3.049	3.00	2.12×10^{-2}
2.5	3.047		
2.0	5.316		
DL-Serine (10^{-2}M)			
10.0	4.876		
5.0	4.090	4.80	3.30×10^{-2}
3.3	3.818		
2.5	3.480		
2.0	5.106		

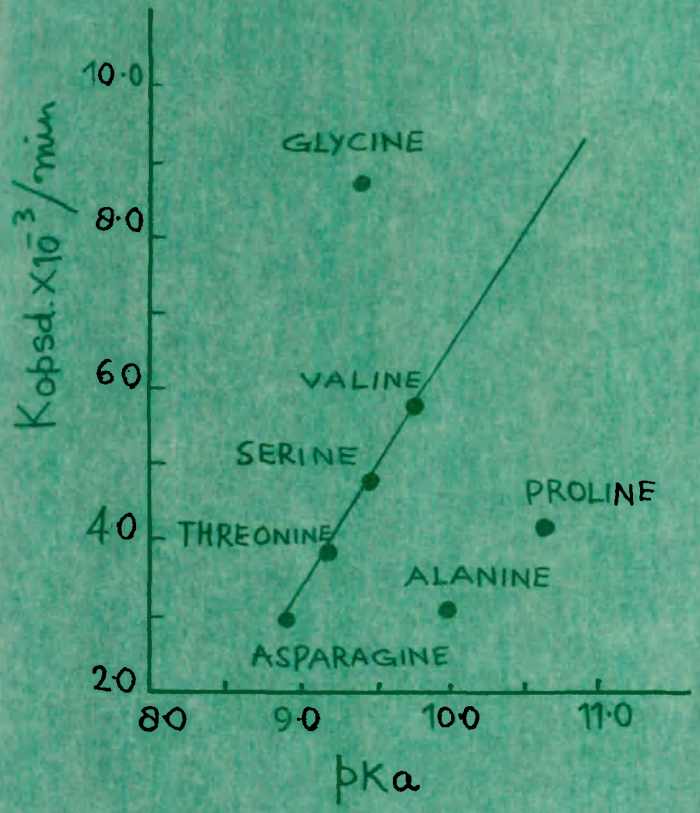
(Contd.)

Aminoacid concentration	$K_{obsd.} \times 10^{-3}$/min	$K_1 \times 10^{-3}$/min	K_2/mole.min.
L-Asparagine (10^{-2}M)			
10.0	2.99		
5.0	3.17		
3.3	4.17	8.70	7.50×10^{-2}
2.5	7.59		
2.0	9.25		
DL-Threonine (10^{-2}M)			
10.0	3.63		
5.0	3.86		
3.3	4.14	3.15	2.00×10^{-2}
2.5	6.21		
2.0	4.21		
DL-Valine (10^{-2}M)			
10.0	5.75		
5.0	5.75		
3.3	5.29	xx	xx
2.5	5.75		
2.0	6.44		
β - Alanine	fast	no	reaction.

(Vide Fig. No.8)

FIGURE NO. 10

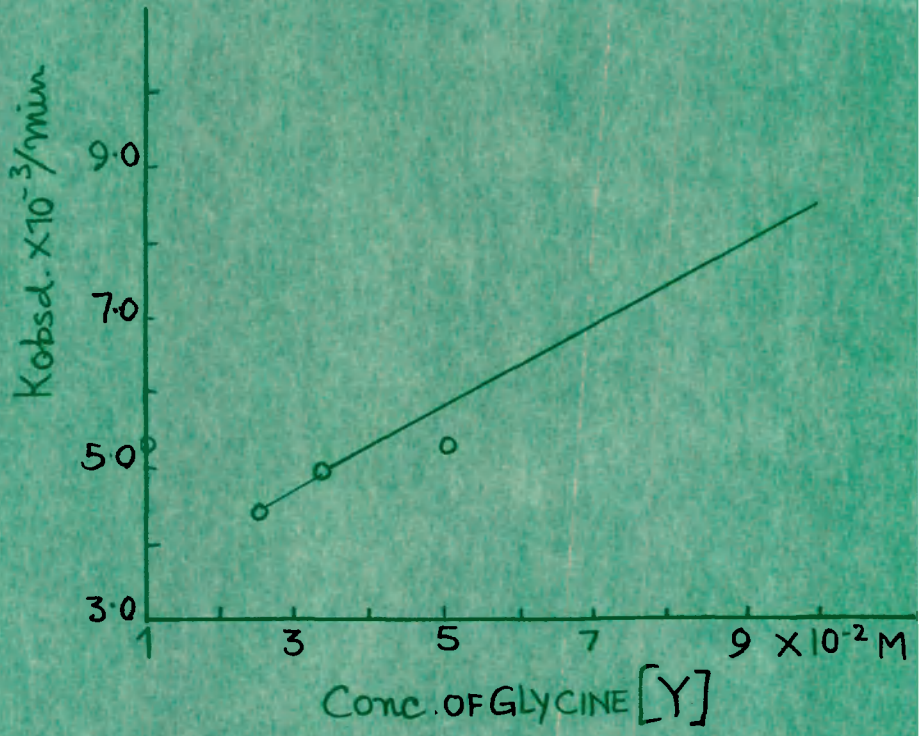
PLOT BETWEEN Kobsd. & pKa



VIDE TABLE NO. 10

FIGURE NO. 8

PLOT BETWEEN Kobsd. & [Y]



VIDE TABLE NO. 8

The values of $K_{obsd.}$ for the various aminoacids follow the order: glycine > DL-valine > DL-serine > L-proline DL-threonine > DL-α-alanine > L-asparagine which roughly corresponds to the order of increasing ionization constants of α-amino carboxylic group e.g., DL-valine > glycine > DL-serine > DL-threonine > L-asparagine > L-proline. Only DL-α-alanine and L-proline deviate from the above order. This indicates the influence of ionization on the extent of substitution of aminoacid in the complex. The plot of $K_{obsd.}$ vs. ionization constants of various aminoacids gives linear relationship for glycine, DL-valine, DL-serine and DL-threonine, L-asparagine belonging to monoaminodicarboxylic class which deviates appreciably from the linear relationship, apparently due to lower ionization constant (Fig.No.9).

The plot of $K_{obsd.}$ vs. pK_a (Fig. No.10) indicates a linear relationship in case of DL-valine, DL-serine, DL-threonine and L-asparagine, appreciable deviation is observed in glycine, DL-α-alanine and L-proline. The departure from the linearity for glycine is due to low pK_a value of glycine in comparison to its immediate analogous, DL-valine, DL-serine and DL-threonine where consistent decrease in pK_a is observed. The fact, that nucleophilic character is some what dependent on pK_a's values, can be demonstrated in these studies, where $K_{obsd.}$ increases with pK_a in case of four aminoacids, DL-valine,

DL-serine, DL-threonine and L-asparagine.

As mentioned above the plot of $K_{obsd.}$ vs. [Y] followed a linear relationship in case of L-asparagine, glycine, L-proline, DL-valine and DL-threonine, the rate law does not hold good. There is no satisfactory explanation for this anomaly, but such type of reactions are well characterised and proceed only with a solvent assisted dissociation mechanism.

The value of the formation constant for the general reaction,

$$[Pd(tu)_4]^{2+} + n[Y]^{-} \overset{-\upsilon - Kf}{\rightleftharpoons} [Pd(tu)_4 \ (Y)_n]^{2-n\upsilon}$$

may be calculated by the spectrophotometric method[19] on following the expression,

$$\log \frac{A_a - A_o}{A_\infty - A_a} = \log K_f + n \log [Y^-]^{\upsilon}$$

where A_a is the absorbance of the complex on addition of the ligand [Y] , A_o is the absorbance with out addition of the ligand [Y] and A_∞ is the absorbance at completion of the reaction. The values of A_a, A_o and A_∞ were determined determined by measuring the absorption of the reaction mixtures containing a fixed concentration of the complex,

$Pd(tu)_4Cl_2$ but varying concentrations of the aminoacid at a constant temperature (35°C) and ionic strength 0.10 (table No.9). The aminoacids used for the studies were L-asparagine, glycine, L-proline DL-valine, DL-α-alanine, DL-serine and DL-threonine. The plot of log $\frac{A_a - A_o}{A_\alpha - A_a}$ versus log [Y] was found to be linear and the values of n, the number of ligands molecules involved in the substitution process and K_f, the formation constant, were computed from the slope and intercept, respectively. In table (No.10) are given the values of log K_f, n and pK_a for the reactions of $Pd(tu)_4Cl_2$ with various aminoacids. The values of DL-serine could not be determined accurately and are, therefore, not included in the present discussion.

T A B L E No.9

Spectrophotometric data for the evaluation of the formation constant (K_f) of the reaction, $[Pd(tu)_4]^{2+} + n[Y]^{\nu} \rightleftharpoons [Pd(tu)_4(Y)_n]^{2-n\nu}$

Aminoacid concentration Glycine(10^{-2}M)	A_a	A_o	A_α	log $\frac{A_a - A_o}{A_\alpha - A_a}$
10.0	0.420	0.04	0.95	-0.1445
5.0	0.275	0.04	0.80	-0.3491
3.3	0.235	0.04	0.70	-0.3775
2.5	0.230	0.04	0.60	-0.3607

(Contd.)

Aminoacid concentration	A_a	A_o	A_α	$\log \frac{A_a - A_o}{A_\alpha - A_a}$
DL-α-Alanine (10^{-2}M)				
10.0	0.280	0.035	1.40	-0.6600
5.0	0.225	0.035	0.95	-0.5815
3.3	0.190	0.035	0.85	-0.6292
2.5	0.150	0.035	0.70	-0.6797
2.0	0.220	0.035	0.52	-0.2099
L-Proline (10^{-2}M)				
10.0	0.210	0.03	0.68	-0.4168
5.0	0.115	0.03	0.52	-0.5106
3.3	0.090	0.03	0.45	-0.7781
2.5	0.090	0.03	0.36	-0.6532
2.0	0.105	0.03	0.29	-0.3921
DL-Serine (10^{-2}M)				
10.0	0.20	0.04	0.75	-0.4394
5.0	0.190	0.04	0.70	-0.5315
3.3	0.185	0.04	0.62	-0.4771
2.5	0.170	0.04	0.43	-0.3011
2.0	0.135	0.04	0.38	-0.4115
L-Asparagine (10^{-2}M)				
10.0	0.165	0.035	0.70	-0.6145
5.0	0.179	0.035	0.65	-0.5509
3.3	0.170	0.035	0.48	-0.3611
2.5	0.170	0.035	0.39	-0.2121

(Contd.)

Aminoacid concentration	A_a	A_o	A_∞	$\log \frac{A_a - A_o}{A_\infty - A_a}$
DL-Threonine (10^{-2}M)				
10.0	0.190	0.04	0.730	-0.5563
5.0	0.185	0.04	0.680	-0.5332
3.3	0.180	0.04	0.605	-0.4823
2.5	0.160	0.04	0.400	-0.3010
2.0	0.130	0.04	0.350	-0.3882
DL-Valine (10^{-2}M)				
10.0	0.310	0.05	0.85	-0.3174
5.0	0.300	0.05	0.80	-0.3011
3.3	0.240	0.05	0.68	-0.3657
2.5	0.235	0.05	0.58	-0.2706
2.0	0.220	0.05	0.48	-0.1846

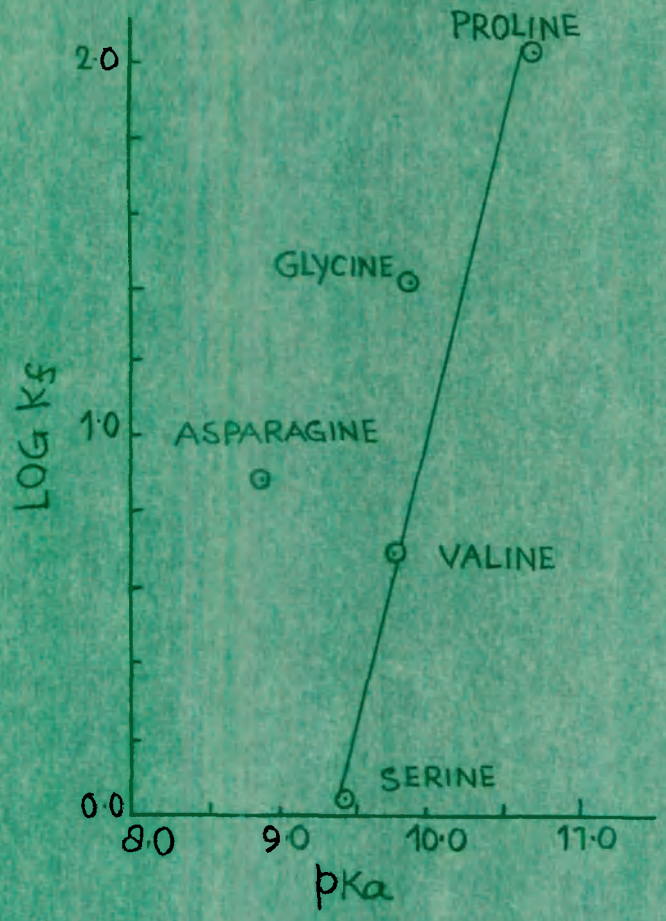
TABLE No.10

Values of n and K_f for the $Pd(tu)_4Cl_2$ and aminoacids complexes.

Aminoacid	log K_f	n	pK_a
L-asparagine	0.8802	1.1	8.85
Glycine	1.4085	1.1	9.86
L-Proline	2.0702	1.7	10.68
DL-Valine	0.6996	0.6	9.72

FIGURE NO. 11

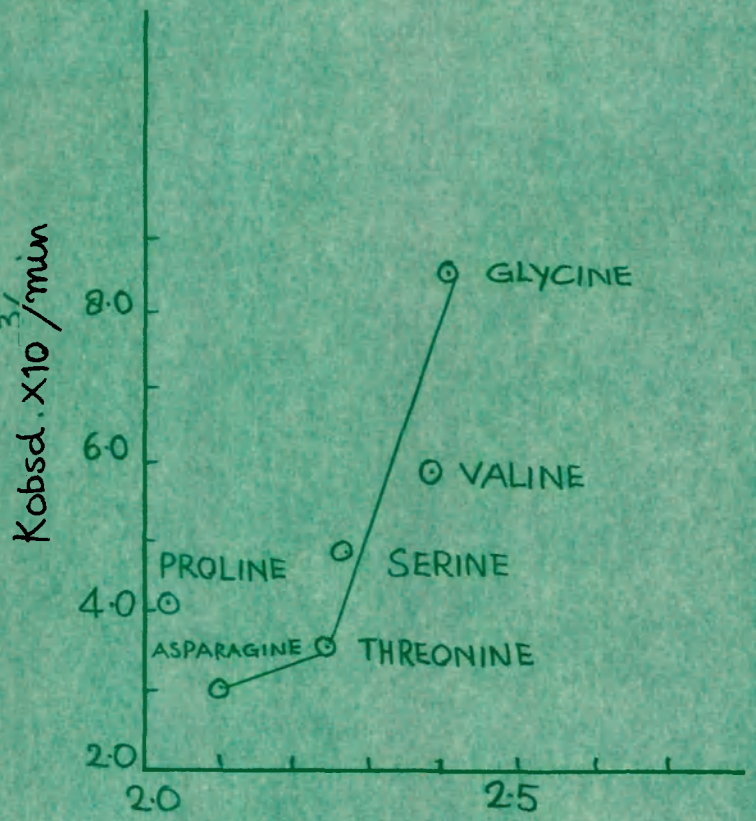
Kf VS. pKa



VIDE TABLE NO. 10

FIGURE NO. 9

Kobsd. Vs IONIZATION CONSTANTS.



VIDE TABLE NO. 8

The plot of log K_f versus pK_a (Fig.No.11) is found to be linear for L-proline, glycine and DL-valine, L-asparagine deviates from the linearity. Such type of plot is similar to that given by Bjerrum for various ligands of the same type interacting with a particular metal, and follow the expression log $K_f = \propto pK_a + C$ where $\propto$ and C are found to be 1.5 and -13.90, respectively.

From the present studies on the substitution reactions of $Pd(tu)_4Cl_2$ with various aminoacids, it is revealed that aminoacids in general, are potential ligands for substitution in Pd(II) square planar complexes. For a reaction of the type, $Pd(tu)_4Cl_2 \overset{+[Y]}{\rightleftharpoons} [Pd(tu)_2(Y)]^+Cl + 2tu$, there is a possibility of the formation of the complex of the type, $[Pd(tu)_2(gly)]$ Cl with the elimination of 2 thiourea molecules. The system studied is first of its kind and indicates the possibility of exploration of the vast yet untouched field of coordination chemistry concerning with the interactions of aminoacid with square planar complexes.

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C H A P T E R - IV:

TRANSITION METAL COMPLEXES OF ALKALOIDS

I N T R O D U C T I O N

Alkaloids are nitrogenous bases with complex structures derived from vegetable origin. Due to their physiological importance, they are widely used in medicines. Most of the alkaloids are highly toxic and their plant extracts have long been used as poisons. They are found to be utilised as antiplasmodial and hypotensive agents, and have analgesic activities. Some of the common alkaloids such as quinine, morphine, cocaine, caffeine and atropeine are so much used in medicines that their applications require no introduction.

Chemically, an alkaloid usually forms an integral part of a cyclic structure. A majority of them are derived from heterocyclic system containining pyridine, pyrrole, tropane, quinoline, iso-quinoline, indole and purine systems.[1] An appreciable number do belong to aliphatic cyclic groups, or a combination of these two, for example cinchona alkaloids, contain aliphatic quinuclidine ring attached to pyridine, quinoline and acridine ring systems, and have been examined for antiplasmodial activity.

The alkaloids are characterised by their basicity arise from the presence of one or more nitrogen atoms in present in aromatic or aliphatic cyclic system together with the presence of various other cyclic or non cyclic substituents groups.

One of the simplest alkaloids, quinaldine is 2-methyl substituted quinoline, whereas quinine consists of two ring systems, a 6-methoxy quinoline and a vinyl substituted quinuclidine ring.[2] Both the ring systems are held together by a secondary alcoholic group-CH(OH). Brucine contains variety of ring systems[3], including indole, bridged 6/6 and 6/5 ring systems, and a seven membered cyclic ether known as oxepine or Δ-3,1, oxacycloheptane, besides methoxy and acylazole groups. Codeine belongs to morphine system[4], contains several rings including a 5-membered cyclic ether and a secondary alcoholic group.

In spite of the tremendous work carried out on alkaloids far last several decades, very little is known about the physical aspects concerning the nature of alkaloids namely, the behaviour of various active groups present, relative basicity of the nitrogen atoms present, their order of nucleophility and spectroscopically, the definite assignments to the bands arising from the group frequencies present in electronic spectra (U.V. and I.R.) of the alkaloids. The study of the coordination chemistry of metal alkaloid complexes requires some intimate knowledge of the properties of the important donor groups present in the compound. Moreover, the availability of the data concerning the assignments to the

various frequencies present in the spectra of the complexes. A simplified course adopted in the present studies concerning with metal-alkaloid interactions is a correlation of the various groups frequency bands of the complexes with those of the alkaloids, attending mainly to the bands produced due to the possible coordination sites.

A limited number of references[5-9] are available in the chemical literature dealing the interactions of transition and non transition metal ions with alkaloids. The metals studied are cadmium, mercury, copper, chromium cobalt and silver etc. The details regarding the work available in literature have already been discussed in the general introduction (pp.17 to 18) and it appears that much has to be investigated in the field of metal - alkaloid complex chemistry, specially keeping in view the structure and bonding at possible coordination sites.

The work described in this chapter includes the syntheses of transition metal complexes of alkaloids, such as quinaldine, quinine, brucine and codeine. The structure of the complexes have been discussed on the basis of infra red spectra. In majority of the complexes the evidences regarding the nature of bonding have been established by comparing the spectra of the alkaloid and the complex, interpreting, the observed changes in the positions of spectral bands upon coordination.

EXPERIMENTAL

Chemicals:- The reagents namely, cupric chloride, cobalt chloride, vanadyl chloride, nickel chloride, chromium chloride, manganese chloride and uranyl sulphate (B.D.H. products) were used. Titanium (III) chloride was prepared as described earlier (chapter, I, p..35).

Alkaloids, such as brucine, quinine and codenine (E.Merck, Germany) were recrystallised before used. Quinaldine (B.D.H. England) was distilled in all Pyrex glass assembly and the distillate collected at its boiling point (246-247°C). Solvents, such as tetrahydrofuran (B.D.H.), methanol, and ether were purified, and distilled before use.

Preparation of the complexes:-

The compounds, reported herein were synthesised from the solutions of metal salts in tetrahydrofuran and appropriate alkaloid solutions in the same solvent. The solution of metal salt was added to the excess of alkaloid's solution with constant stirring. The precipitate was washed several times with solvent to remove the excess of the metal ion and alkaloid. The compounds were dried over anhydrous calcium chloride in vacuum.

Apparatus:- I.R. spectra of brucine, quinine and quinaldine complexes were recorded with Perkin-Elmer Model 21 spectrophotometer, using KBr phase. In case of codeine, the spectra recorded with Beckman Model BK 56(10441) spectrophotometer, using nujol-mul with CsI.

Analytical data for quinaldine-metal chelates

(1) $Ti(QD)_2Cl_3 2H_2O$:- Yellow product, m.p.204-205°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, ether, $CHCl_3$, THF etc.

Cald.for $C_{20}H_{18}N_2 TiCl_3 2H_2O$

	C	H	N	Ti	Cl^-
Calculated:	50.40	4.61	5.88	10.86	22.35
Found:	49.48	4.74	5.78	10.66	22.21

(2) $VO(QD)_2Cl_2 2H_2O$:- Gray coloured product, m.p.149-150°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, ether, $CHCl_3$ THF etc.

Cald.for $C_{20}H_{18}N_2VOCl_2 2H_2O$.

	C	H	N	V	Cl^-
Calculated:-	51.76	4.74	6.04	10.99	15.29
Found:-	51.84	4.89	6.00	11.25	15.42

(3) $UO_2(QD)_2SO_4$:- Dark yellow coloured product, m.p. above 360°C, soluble in water but insoluble in organic solvents such as alcohol, acetone, ether, $CHCl_3$, THF etc.

Cald.for $C_{20}H_{18}N_2 UO_2SO_4$.

	C	H	N	U	SO_4^{--}
Calculated:-	36.78	2.76	4.29	36.41	14.71
Found:-	36.94	2.88	4.32	36.63	14.90

QD = $C_9H_6NCH_3$ (Quinaldine)

Following are the positions and intensities of the various bands present in the spectra of quinaldine and its complexes.

Quinaldine

3350(m), 3000(m), 1625(s), 1600(v.s.) 1570(m), 1500(v.s), 1425(s), 1375(v.s), 1310(v.s), 1225(v.s), 1150(s), 1110(v.s), 955(m), 875(v.w), 825(m), 790(m), 750(s).

(Vide plate No.1)

Quinaldine $TiCl_3$ complex

3200(b), 3000(w), 2600(v.s), 1900(m.s), 1650(s), 1590(m), 1500(m), 1410(v.s), 1380(v.s), 1300(s), 1220(v.s), 1143(s), 1040(m), 970(s), 885(m), 850(v.s),775(v.s).

(Vide plate No.2)

Quinaldine- $VOCl_2$ Complex

3600(s), 2950(m), 2700(m), 2380(s), 1650(v.s), 1500(v.s), 1450(s), 1420(s), 1290(s), 1220(m), 1200(s), 1115(s),1080(m), 1060(m), 1030(m), 1013(m), 985(m) , 850(m), 785(w), 765(m).

(Vide plate No.3)

Quinaldine - UO_2SO_4 complex

3500(m&b), 3000(w), 1650(v.s), 1600(s), 1550(m), 1430(m.s), 1380(s), 1300(m), 1150(w.b), 1125(m), 1075(s), 930(w), 830(m), 780(m).

(Vide plate No.4)

T A B L E No.1.

Assignments to characteristic infra red frequencies of quinaldine and its complexes.

	CH stretching	CC,CN ring stretching	CH in plane deformation	Ring skeletal	CH out of plane.
	3000 cm^{-1}	1600-1300cm^{-1}	1300-1100cm^{-1}	900cm^{-1}	800cm^{-1}
Quinaldine	3000 (m)	1625(s),1600(v.s)	1310(s)	955 (m)	825 (m)
		1570(m),1500(v.s),	1225(v.s)		790 (m)
		1425(s),1375(v.s)	1150(s)		750 (s)
			1110(v.s)		
Quinaldine	3000 (m)	1650(v.s),1590(m)	1300(s),1220(v.s)	970(s)	855(m)
$TiCl_3$Complex	2600 (v.s)	1500(m),1410(v.s)	1143(s),1040(m)		850(v.s)
		1380 (v.s)			755(v.s)
Quinaldine	2950 (m)	1650(v.s),1500(v.s)	1290(s),1220(m)		
$VOCl_2$Complex	2700 (m)	1450(s) 1420(s)	1200(s),1115(s)	985(m)	
			1080(m),1060(m)		850(m)
			1030(m),1013(m)		785(w)
					765(m)
Quinaldine	3000(w)	1650(v.s),1600(s)	1300(m),1150(w), 1125(m)	930(w)	780(m)
UO_2SO_4complex		1550(m),1430(m.s) 1380(s)	1075(s)		

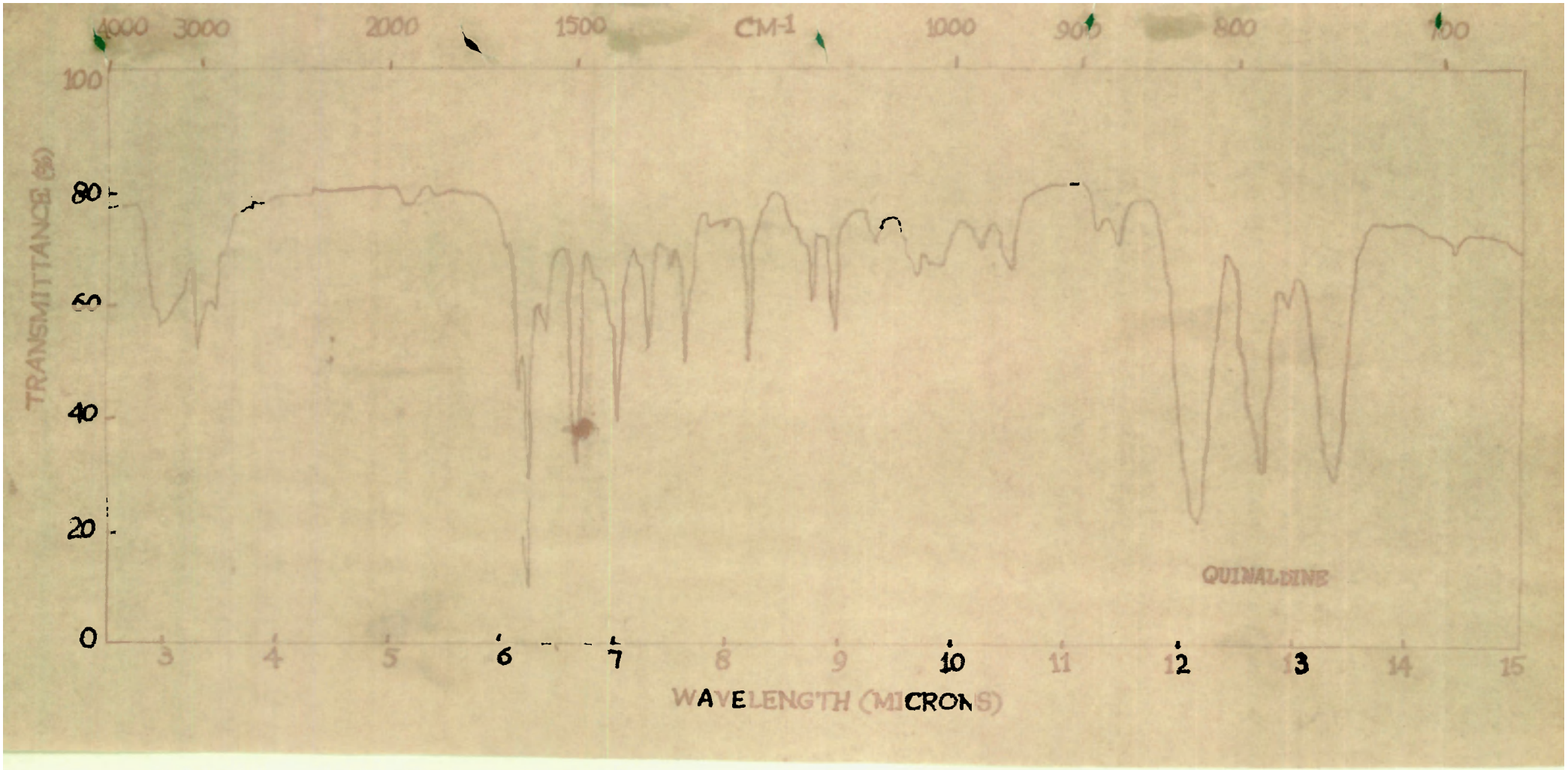

Plate No.1 - I.R. Spectra of Quinaldine

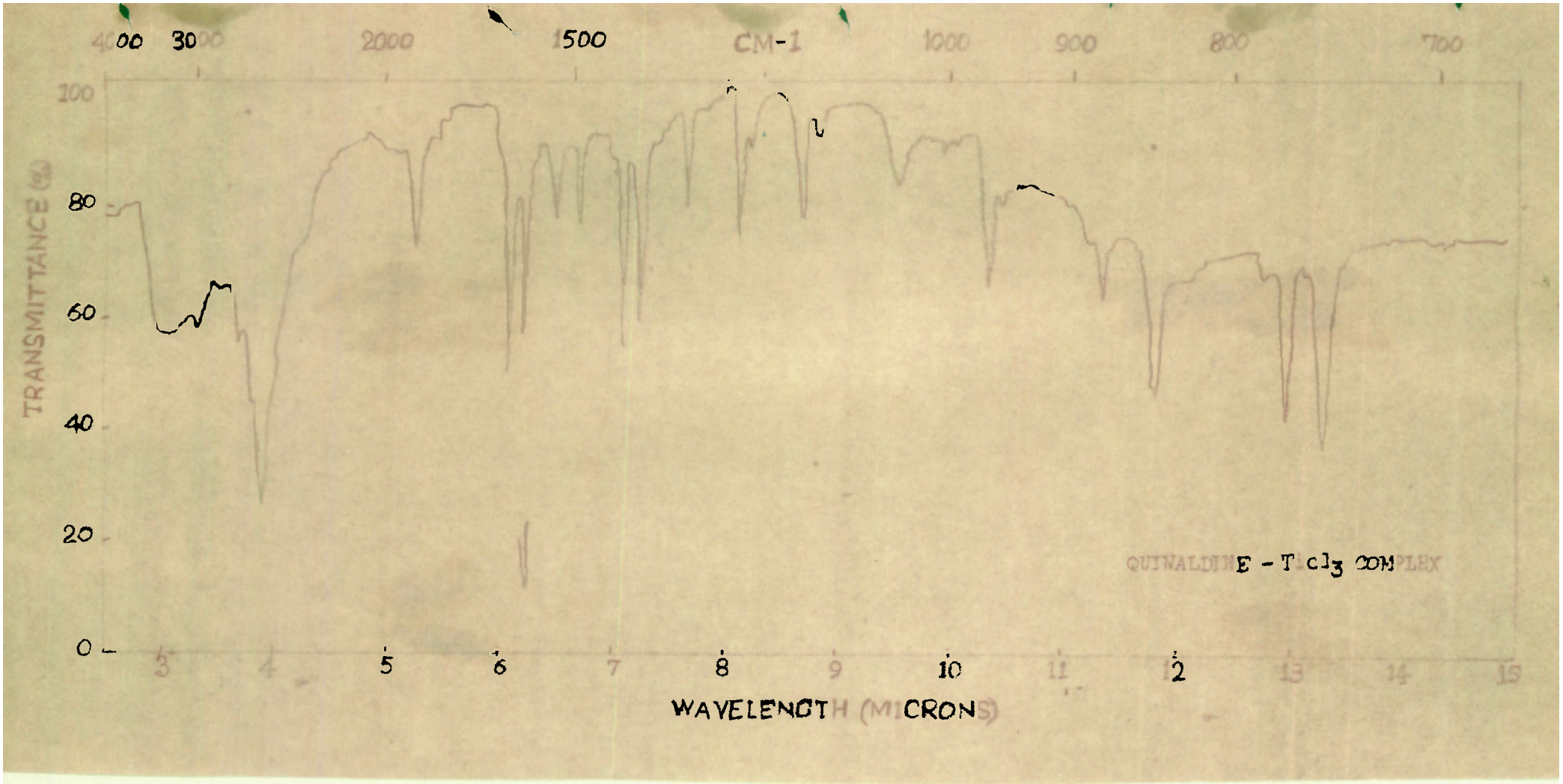

Plate No.2 - I.R. Spectra of Quinaldine - $TiCl_3$ complex.

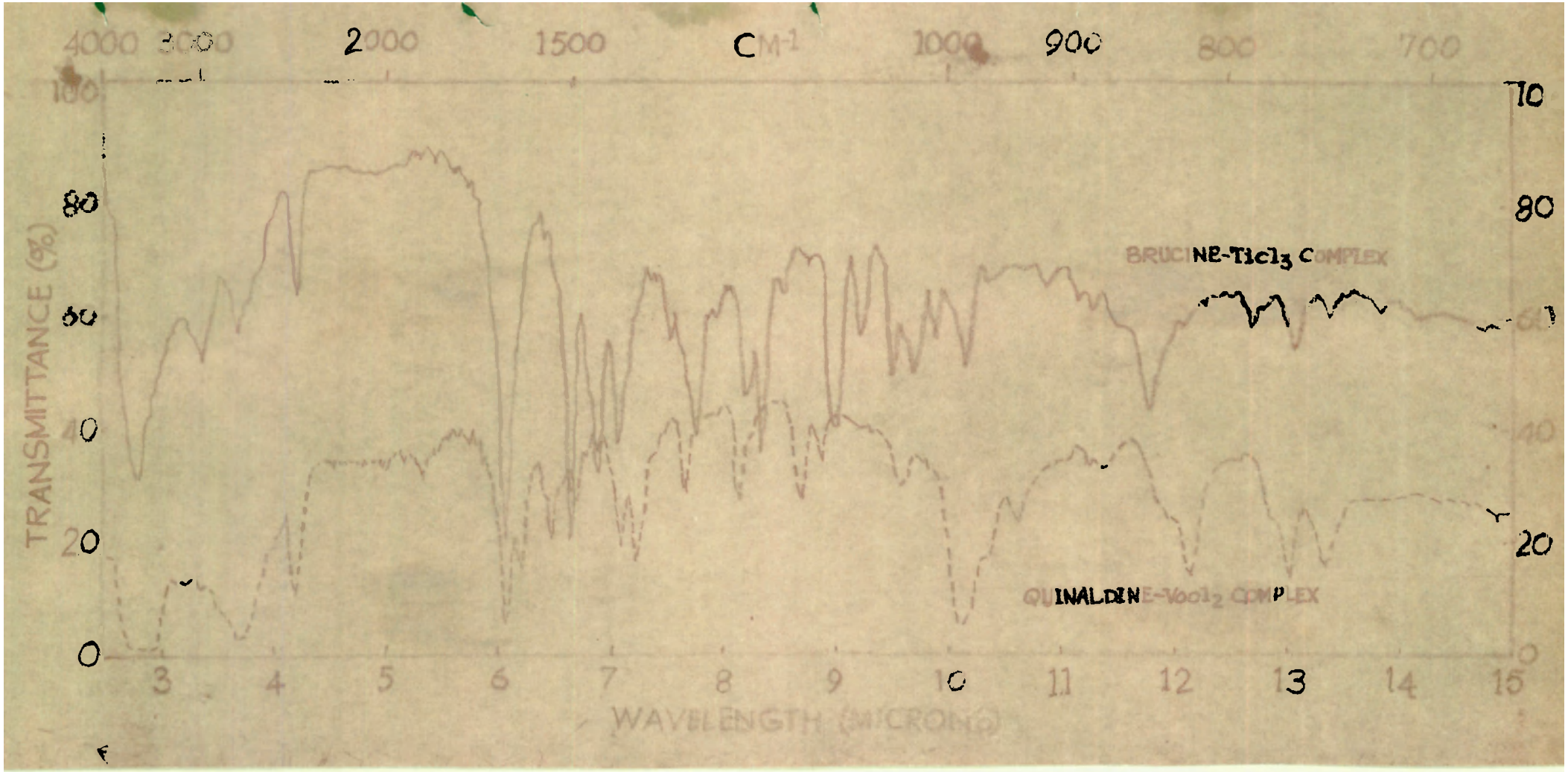

Plate No.3 - I.R. Spectra of Quinaldine-$VOCl_2$ complex

" " - I.R. Spectra of Brucine - $TiCl_3$ complex

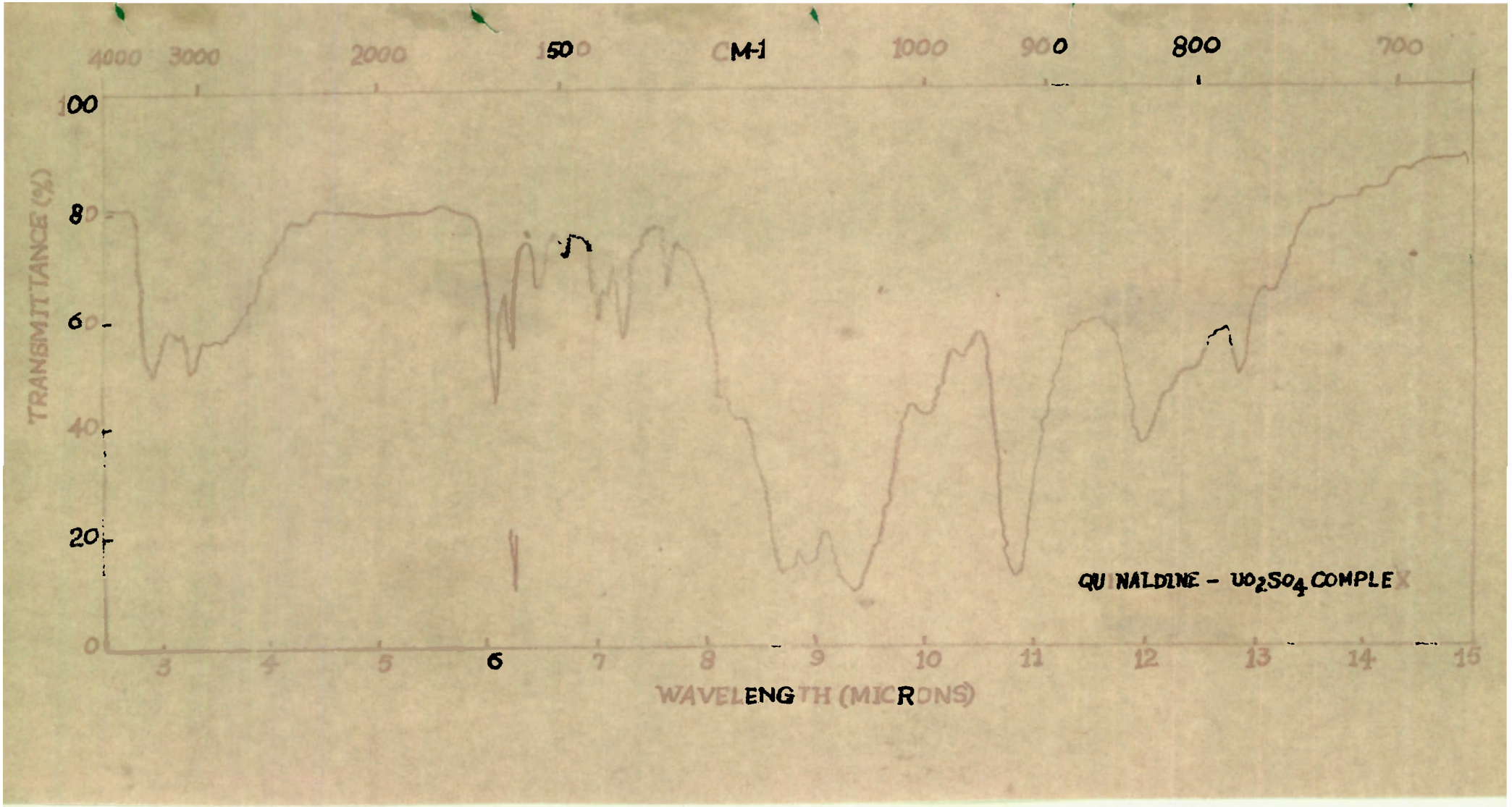

Plate No.4 - I.R. Spectra of Quinaldine-UO_2SO_4 complex

Analytical data for quinine-metal chelates

(1) $Ti(Quin)Cl_3 2H_2O$:- Mustard coloured product, m.p.242-243°C, hygroscopic, soluble in water, but insoluble in organic solvents such as alcohol, acetone, ether, $CHCl_3$, THF etc.

Cald. for $C_{20}H_{24}O_2N_2\ TiCl_3\ 2H_2O$

	C	H	N	Ti	Cl^-
Calculated:	46.67	5.44	5.44	9.28	9.28
Found:	46.82	5.60	5.48	9.40	9.39

(2) $VO(Quin)Cl_2 2H_2O$:- Steel grey coloured product, m.p.232-233°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, ether, $CHCl_3$ THF etc.

Cald. for $C_{20}H_{24}O_2N_2\ VOCl_2\ 2H_2O$.

	C	H	N	V	Cl^-
Calculated:-	48.22	5.76	5.60	10.44	16.14
Found:-	48.02	5.90	5.48	10.60	16.24

Quin = $C_{20}H_{24}O_2N_2$ (Quinine)

Following are the positions and intensities of the various bands present in the spectra of quinine and it complexes.

Quinine

3650(s), 3350(m), 3200(m), 2700(m), 1640(s), 1500(s),1475(s), 1430(v.s), 1360(m), 1330(m), 1240(vs), 1225(s), 1195(s), 1130(m&b), 1090(m), 1040(m), 1025(m), 975(m), 925(s), 880(m), 855(m), 835(m), 800(m&b), 715(m), 695(w&b).

(Vide plate No.5)

Quinine - $TiCl_3$ complex.

3560(m), 3000(m), 2400(m), 1635(m), 1610(sh), 1555(sh),1500(m), 1460(m), 1425(m), 1390(m), 1250(s), 1170(m&b), 1100(m),1010(sh), 990(m), 850(m&b), 760(w&b), 715(w).

(Vide plate No.6)

Quinine - $VOCl_2$ complex

3560(m), 3000(m), 2400(m), 1635(m), 1610(m), 1550(m),1500(m), 1460(m), 1430(m), 1390(m), 1225(m), 1170(m&b), 1100(m), 1095(m&b), 920(m&b), 855(m&b), 715(w&b).

(Vide plate No.6)

TABLE No.2:

Assignments to characteristic infra red frequencies of quinine and its complexes

Compounds	OH, stretching (secondery)	CH, stretching	Quinoline ring CC, CN	CN, stretching of quinuclidine	CO, stretching methoxy	C-OH stretchi
Quinine	3650	3200, 2700	1640, 1500, 1475	1040	1195	1090
Quinine $-TiCl_3$ complex	3560	3000, 2400	1635, 1510, 1555 1500, 1460	1010(sh)	1170	1100
Quinine-$VOCl_2$ Complex	3560	3000, 2400	1635, 1610, 1550 1500, 1460, 1430	1020	1170	1095

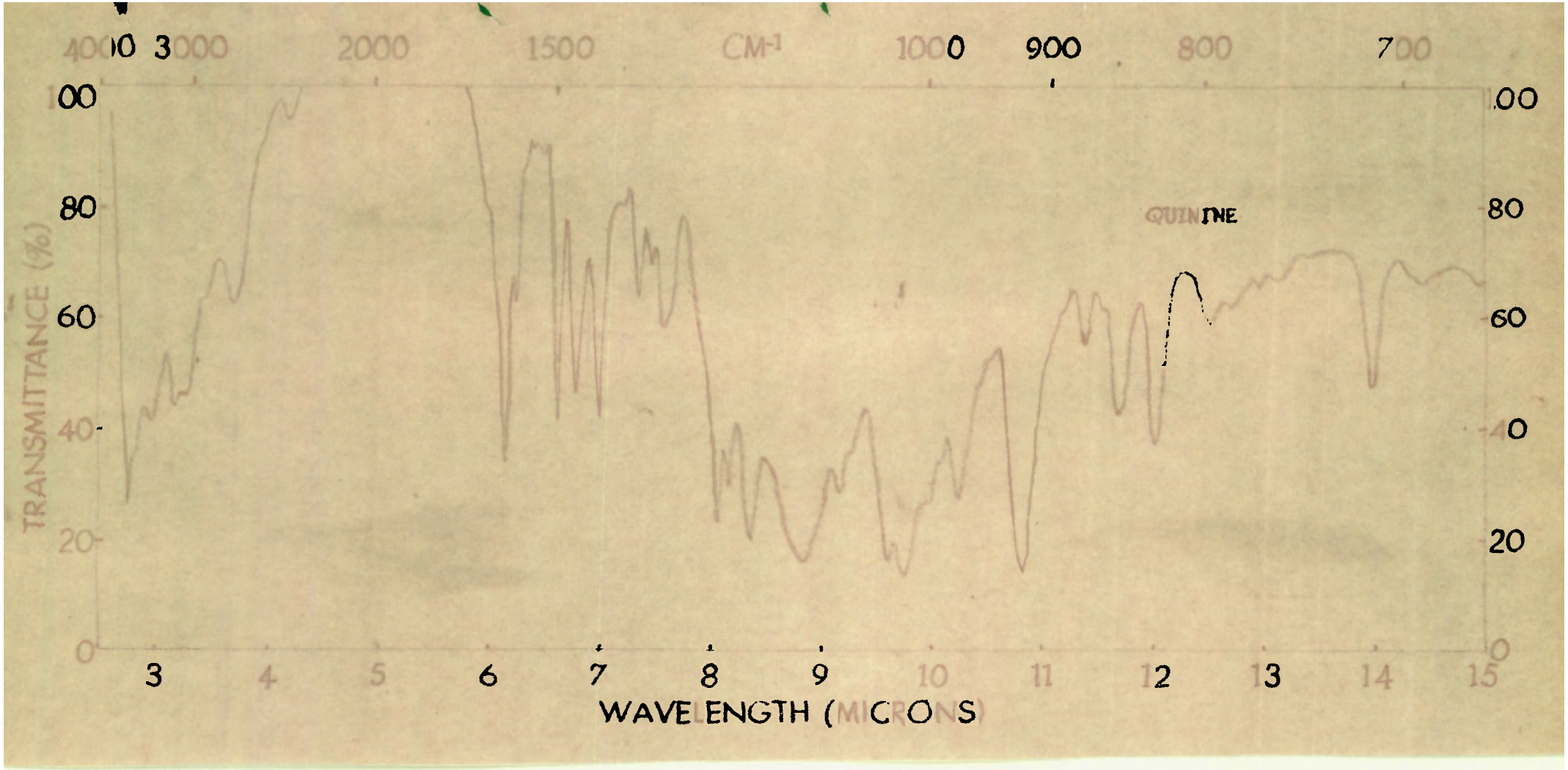

Plate No.5 - I.R. Spectra of Quinine

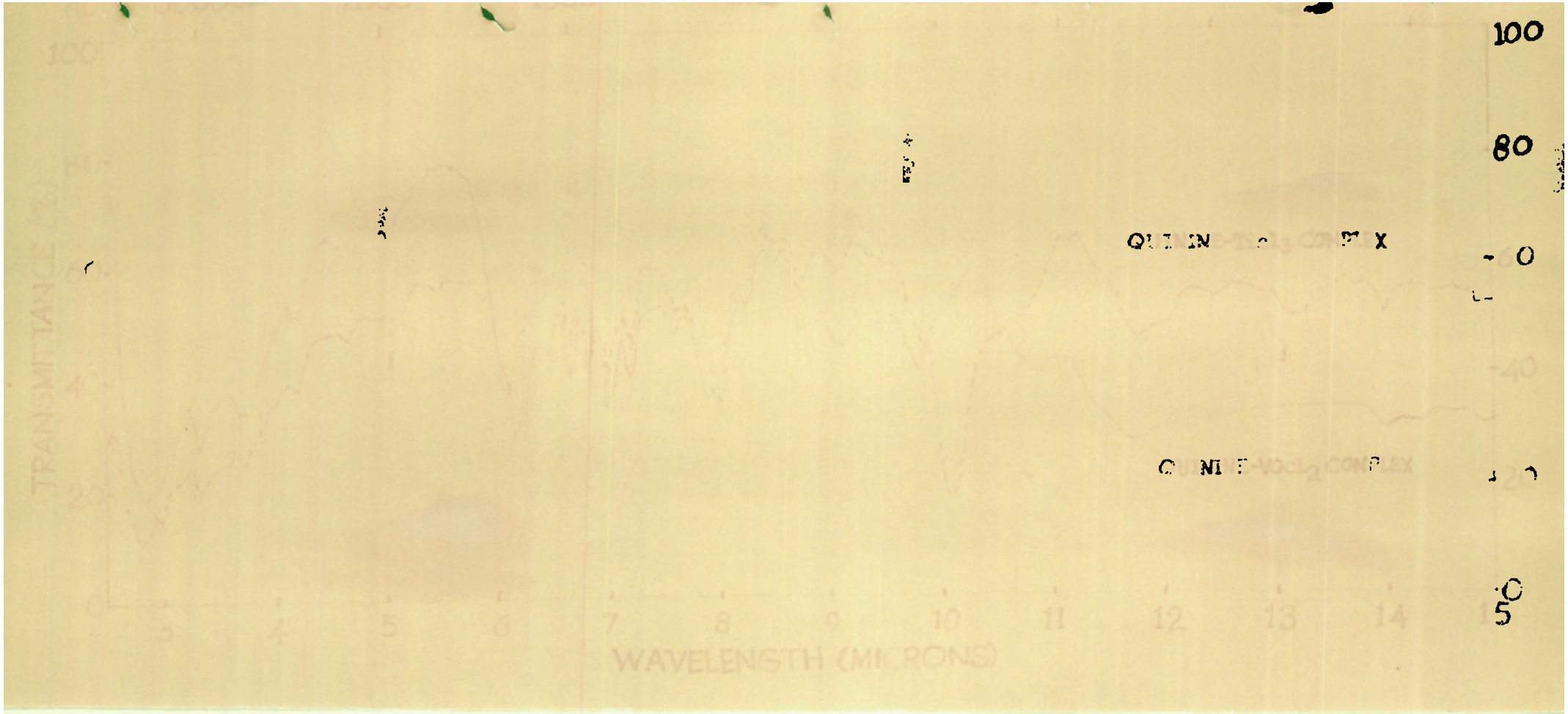

Plate No.6 - I.R. Spectra of Quinine-$FiCl_3$ complex

" " I.R. Spectra of Quinine-$VOCl_2$ complex

Analytical data for Brucine-metal chelates

(1) $VO(Bru)Cl_2\ 2H_2O$:- Gray product, m.p. above 360°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald. for $C_{23}H_{26}O_4N_2VOCl_2 2H_2O$

	C	H	N	V	Cl^-
Calculated:-	45.70	4.96	4.63	8.44	11.74
Found:-	45.54	4.78	4.52	8.32	11.85

(2) $Ti(Bru)Cl_3 2H_2O$:- Light yellow product, m.p. 279-280°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald. for $C_{23}H_{26}O_4N_2\ TiCl_3 2H_2O$

	C	H	N	Ti	Cl^-
Calculated:-	47.24	5.14	4.79	8.18	18.3
Found:-	47.36	5.27	4.69	8.25	18.5

(3) $UO_2(Bru)SO_4 2H_2O$:- Dark yellow product, m.p. above 360°C, soluble in water but insoluble in organic solvents such as alcohol, acetone, $CHCl_3$, THF, etc.

Cald. for $C_{23}H_{26}O_4N_2\ UO_2SO_4 2H_2O$

	C	H	N	U	SO_4^{--}
Calculated:-	41.31	4.49	4.19	35.57	14.37
	41.50	5.05	4.22	35.70	14.50

Bru = $C_{23}H_{26}O_4N_2$ (Brucine)

Following are the positions and intensities of the various bands present in the spectra of brucine and its complexes.

Brucine

3600(m&b), 3000(m&b), 2850(m), 1675(s), 1665(s), 1625(m), 1450(s), 1400(w&b), 1335(m), 1275(m&b), 1200(s), 1125(v.s), 1090(sh), 1075(w), 1050(w), 1030(w&b), 1010(m), 995(m), 940(m), 920(m), 850(m), 840(m), 790(m), 760(m), 705(w).

(Vide plate No.7)

Brucine-$VOCl_2$ complex

3600(m), 3000(w), 2700(w&b), 238(m), 1675(s), 1660(s), 1500(s), 1450(s), 1425(m), 1400(m), 1275(s), 1215(m), 1200(m), 1112(s), 1075(m), 1050(m), 1040(m), 985(m&b), 848(w), 765(w), 750(w).

(Vide plate No.7)

Brucine-$TiCl_3$ complex

3600(m), 2950(m), 2700(m&b), 2375(m), 1660(s), 1500(s), 1450(s), 1425(m&b), 1295(m&sh), 1225(m), 1200(v.s), 1110(s), 1075(m), 1050(m), 1035(m&b), 1018(m), 985(m), 850(m), 785(w), 765(m), 752(w), 725(w).

(Vide plate No.3)

Brucine-UO_2SO_4 complex

3600(s), 3000(m), 2700(m), 2340(m&s), 1660(s), 1560(m), 1510(s), 1450(s), 1410(m&sh), 1360(w), 1290(s), 1260(w), 1215(m), 1200(s), 1140(w), 1115(m&sh), 1080(m), 1055(m), 1035(m&b), 1020(m), 988(m), 970(w), 900(w), 87(w), 845(m&sh), 828(w), 788(m), 775(m&sh), 750(m), 740(w), 738(w).

(Vide plate No.8)

T A B L E No.3:

Assignments to characteristic infra red frequencies of brucine and its complexes

Compound	CH, stretching	C=C stretching	CO, stretching of acylazole	CN, stretching of acylazole	CN stretching 5/6 pyrrocoline ring	$-OCH_3$ stretching	CO,CC stretching of oxepine ring
Brucine	3000cm^{-1}	1665cm^{-1}	1626cm^{-1}	1335cm^{-1}	1090cm^{-1}	1200cm^{-1}	1450cm^{-1}
VO^{2+}Complex	3000cm^{-1}	1660cm^{-1}	-	-	1075cm^{-1}	1200cm^{-1}	1450cm^{-1}
Ti^{3+}complex	3000cm^{-1}	1660cm^{-1}	-	-	1075cm^{-1}	1200cm^{-1}	1450cm^{-1}
UO_2^{2+} Complex	3000cm^{-1}	1660cm^{-1}	-	-	1080cm^{-1}	1200cm^{-1}	1450cm^{-1}

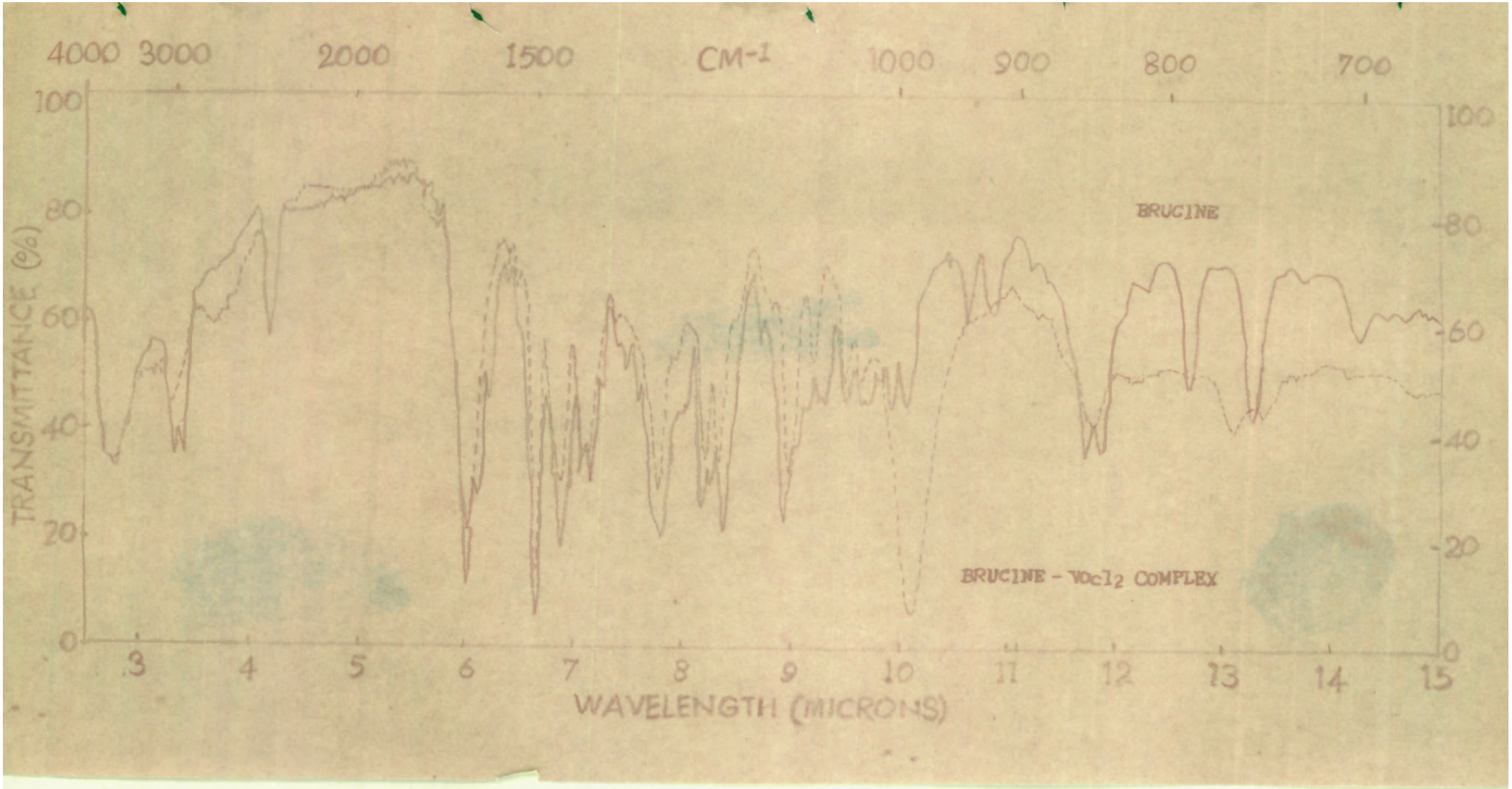

Plate No. 7 - I.R. Spectra of Brucine

" " - I.R. Spectra of Brucine - $VOCl_2$ complex

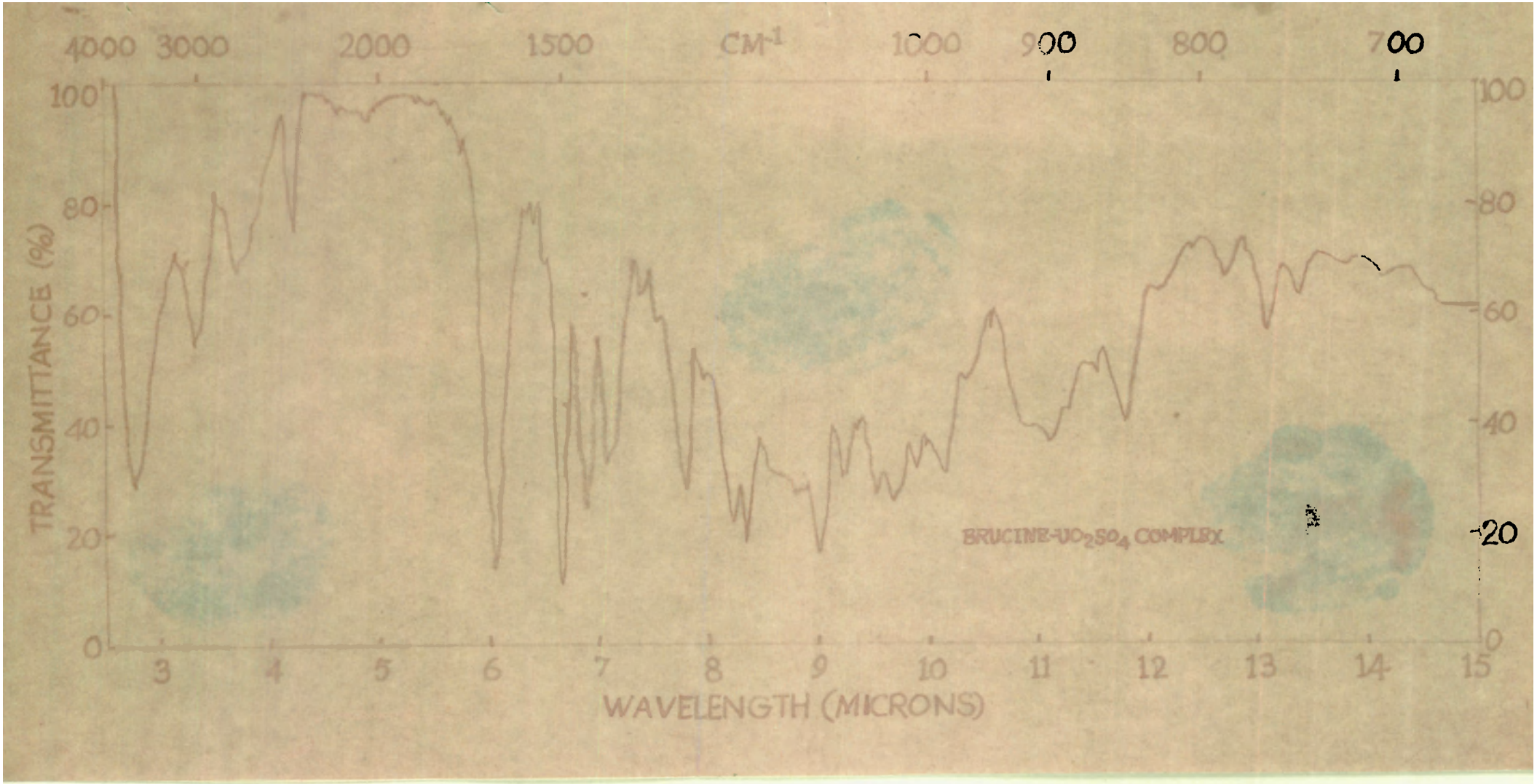

Plate No.8 - I.R. Spectra of Brucine - UO_2SO_4 complex

Analytical data for codeine-metal chelates

(1) $Cu(Cod)_2Cl_2\ 2H_2O$:- Mustard coloured product, m.p.156-157°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald.for $C_{36}H_{42}O_6N_2CuCl_2 2H_2O$

	C	H	N	Cu	Cl
Calculated:-	56.21	5.90	3.60	8.25	9.25
	56.36	5.76	3.52	8.02	9.28

(2) $Co(Cod)_2Cl_2 2H_2O$:- Bluish green product, m.p. 218-219°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald.for $C_{36}H_{42}O_6N_2COCl_2 2H_2O$

	C	H	N	Co	Cl
Calculated:-	57.08	6.02	3.66	7.74	9.49
Found:-	56.90	6.30	3.62	7.76	9.54

(3) $Ti(Cod)_2Cl_3 2H_2O$:- Dirty yellow product, m.p. 271-272°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, etc.

Cald.for $C_{36}H_{42}O_6N_2\ TiCl_3 2H_2O$

	C	H	N	Ti	Cl
Calculated:-	55.40	5.97	3.16	2.54	13.49
Found:-	55.32	6.04	3.12	2.48	13.60

(Contd.)

(4) $VO(Cod)_2Cl_2 2H_2O$:- Dark gray product, m.p.149-150°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald.for $C_{36}H_{42}O_6N_2VOCl_2 2H_2O$.

	C	H	N	V	Cl^-
Calculated:-	55.98	5.96	3.62	6.59	9.18
Found:-	55.88	6.12	3.60	6.72	9.30

(5) $Ni(Cod)_2Cl_2 2H_2O$:- Light green, m.p. 149-150°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, THF, $CHCl_3$ etc.

Cald.for $C_{36}H_{42}O_6N_2NiCl_2 2H_2O$

	C	H	N	Ni	Cl^-
Calculated:-	57.10	6.08	3.68	7.76	9.51
Found:-	57.30	6.18	3.65	7.82	9.94

(6) $Cr(Cod)_2Cl_3 2H_2O$:- Very light green product, m.p. above 360°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, $CHCl_3$, THF etc.

Cald.for $C_{36}H_{42}O_6N_2CrCl_3 2H_2O$

	C	H	N	Cr	Cl^-
Calculated:-	54.53	5.81	3.66	6.56	13.42
Found:-	54.60	6.25	3.71	6.77	13.56

(7) $Mn(Cod)_2Cl_2$:- Light pink product, m.p. 254-205°C, hygroscopic, soluble in water but insoluble in organic solvents such as alcohol, acetone, $CHCl_3$, THF etc.

Cald.for $C_{36}H_{42}O_6N_2MnCl_2$

	C	H	N	Mn	Cl^-
Calculated:-	56.88	6.05	3.68	7.22	9.33
Found:-	56.68	6.20	3.62	7.10	9.50

Cod = $C_{18}H_{21}O_3N$ (Codeine)

Following are the positions and intensities of the various bands present in the spectra of codeine and its complexes.

Codeine

3600(m), 3580(w), 3460, 3120(w), 2710(w), 1900(w), 1630(s), 1605(s), 1440(m&b), 1370(m), 1300(m), 1265(m), 1200(m), 1150(m), 115(m), 1045(m&sh), 970(m), 935(m), 835(s), 780(s), 750(s), 710(m), 640(s), 625(m), 620(m), 610(m), 570(m), 500(s), 460(m), 395(m), 350(m&b), 270(m),

(Vide plate No.9)

Codeine - $NiCl_2$ complex

3530(m), 3495(w), 3420(w), 3320(m), 3220(m&b), 2910(m&b), 2840(b), 2760(w), 2710(w), 2615(w), 2575(w), 2475(w), 2360(m), 1646(m), 1605(m), 1500(s), 1460(m&b), 1375(s), 1325(m), 1275(m&sh), 1200(m), 1160(m), 1130(m), 1115(m), 1085(m), 1070(m), 1045(m), 1015(m), 970(m), 945(m), 915(m), 870(m), 840(m), 800(m), 790(m), 750(m), 720(m), 695(m), 610(w), 600(m&b), 450(m), 315(w),

(Vide plate No.10)

Codeine - $CuCl_2$ complex

3530(w), 3450(w), 3350(w&sh), 2905(m&b), 2840-2980(b), 2760(w), 2730(w), 1635(m&sh), 1605(m), 1510(s), 1460(m&b), 1375(s), 1270(m&sh), 1190(m&sh), 1160(m), 1130(s), 1065(m&b), 1045(m&sh), 1015(m), 975(m), 935(m&sh), 915(m), 865(m), 825(m), 785(m&sh), 750(m), 720(m), 555(m&b), 325(w), 275(w).

(Vide plate No.11)

(Contd.)

Codeine - $VOCl_2$ complex

3640(m&b), 3410(w), 2950(w), 2930(w), 2900-2840(b), 2780-2730(b), 1670(m), 1640(s), 1605(s), 1185(w), 1065(w), 1035(m), 970(m&b), 940(m&sh), 915(s), 865(s), 835(m), 785(s), 750(m), 715(m), 690(m), 670(w), 605(w), 595(m&b), 445(m&b), 340(w), 315(w), 275(m).

(Vide plate No.12)

Codeine - $COCl_2$ complex

3560(w), 3420(w&b), 2980-2830(b), 2730(w), 1635(m), 1605(m), 1500(s), 1445(m&b), 1375(s), 1270(m&sh), 1190(m&sh), 1160(m), 1125(s), 1065(w), 1045(m), 975(m), 935(m&b), 870(m), 830(m), 785(m), 750(w), 715(m), 615(w), 320(w), 295(w&sh).

(Vide plate No.13)

Codeine - $MnCl_2$ complex

3530(w), 3420(w), 3220(w), 2840-3000(b), 2770(w), 2730(w), 1640(s), 1605(s), 1450(m&b), 1375(m&sh), 1270(s), 1125(m), 1180(s), 1115(s), 1070(s), 1045(m), 970(s), 935(m), 915(m), 870(m), 835(m), 780(m), 750(m), 730(m), 695(m), 595(m), 510(m), 455(m), 316(w), 270(m).

(Vide plate No.14)

Codeine - $CrCl_3$ complex

2830(w), 2730(w), 2460(w), 1980(w&b), 1670(m), 1630(w), 1605(s), 1500(v.s), 1450(m&b), 1380(s), 1325(m), 1270(s), 1180(v.s), 1115(s), 1075(m), 1040(m), 1020(m), 970(m), 935(m), 920(m), 870(m), 835(m), 785(s), 755(m), 720(m), 695(m), 625(m), 310(w), 275(m).

(Vide plate No.15)

Codeine - $TiCl_3$ complex

3580(w), 3440(w), 3040-2830(b), 2920(m&b), 2730(w), 1960(w), 1640-1630(b), 1605(s), 1450(m&b), 1380(m), 1325(m), 1265(s), 1225(m), 1190(s), 1115(v.s), 1045(m), 1015(s), 970(s), 935(m), 915(m), 870(m), 830(m), 780(m), 755(m), 730(m), 695(m), 595(m), 455(m), 315(w).

(Vide plate No.16)

TABLE NO.4.

Assignments to characteristic infra red frequencies of codeine and its complexes

Compound	CH stretching	CH_3N stretching	C=C stretching	Dihydro furan ring stretching	Dihydro furan CH in plane deformation	Dihydro furan CH out of plane deformation
Codeine	3120(w)	2710(w)	1630	1605	1265	835,750
Ni^{2+}-Codeine Complex	2840-2980 (b)	2760,2710	1646	1605	1275	840,750
Cu^{2+}-Codeine Complex	2840-2980 (b)	2760,2730	1635	1605	1270	835,750
VO^{2+}-Codeine Complex	2930,2950	2730,2780	1610	1605	1270	835,750
Co^{2+}-Codeine Complex	2830-2980 (b)	2730	1635	1605	1270	830,750
Mn^{2+}-Codeine Complex	2840-3000 (b)	2730,2770	1640	1605	1270	835,750
Cr^{3+}-Codeine Complex	2830	2735	1630	1605	1270	835,755
Ti^{3+}-Codeine Complex	2830,3040 (b)	2730	1630-1640 (w)	1605	1265	830,755

T A B L E No.4 (Contd.)

Assignments to characteristic infra red frequencies of codeine and its complexes

Compound	OH stretching	$-OCH_3$ stretching	C-OH stretching	C-N stretching	Dihydro furan ring skeletal	M-Cl stretching
Codeine	3580	1200	1070	1045	970	x
Ni^{2+}-codeine complex	3530	1200	1070	1045	970	315(w)
Cu^{2+}-Codeine complex	3530	1190	1065	1045	975	325(w)
VO^{2+}-Codeine complex	-	1185	1065	1035	970	315
CO^{2+}-Codeine complex	-	1190	1065	1045	975	320(w)
Mn^{2+}-Codeine complex	3530	1180	1070	1045	970	315
Cr^{3+}-Codeine Complex	-	1180	1075	1040	970	310
Ti^{3+}-Codeine Complex	3580	1190	1075	1045	970	315

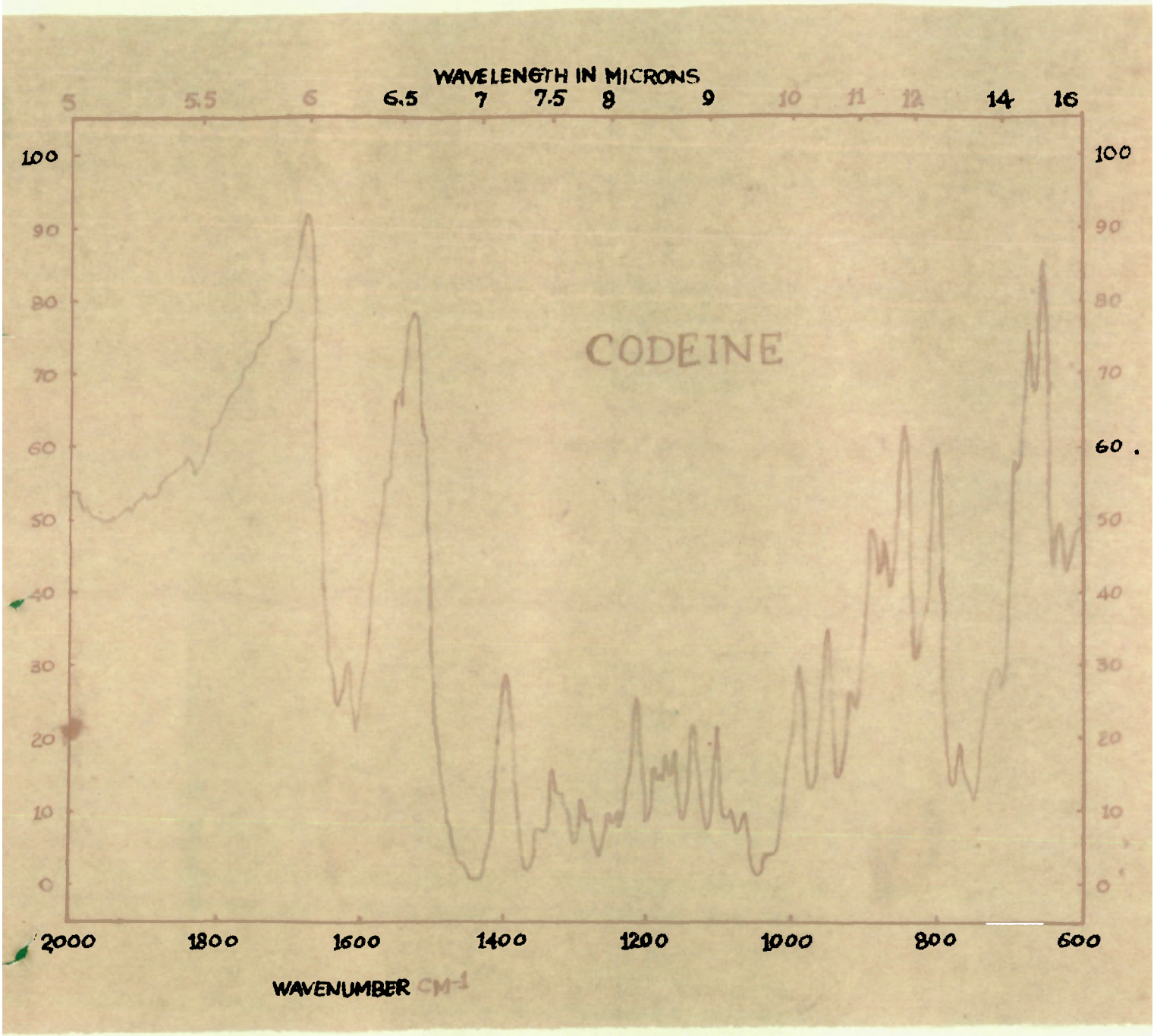

Plate No.9 - I.R. Spectra of Codeine

Plate No.10 - I.R. Spectra of Codeine-$NiCl_2$ complex

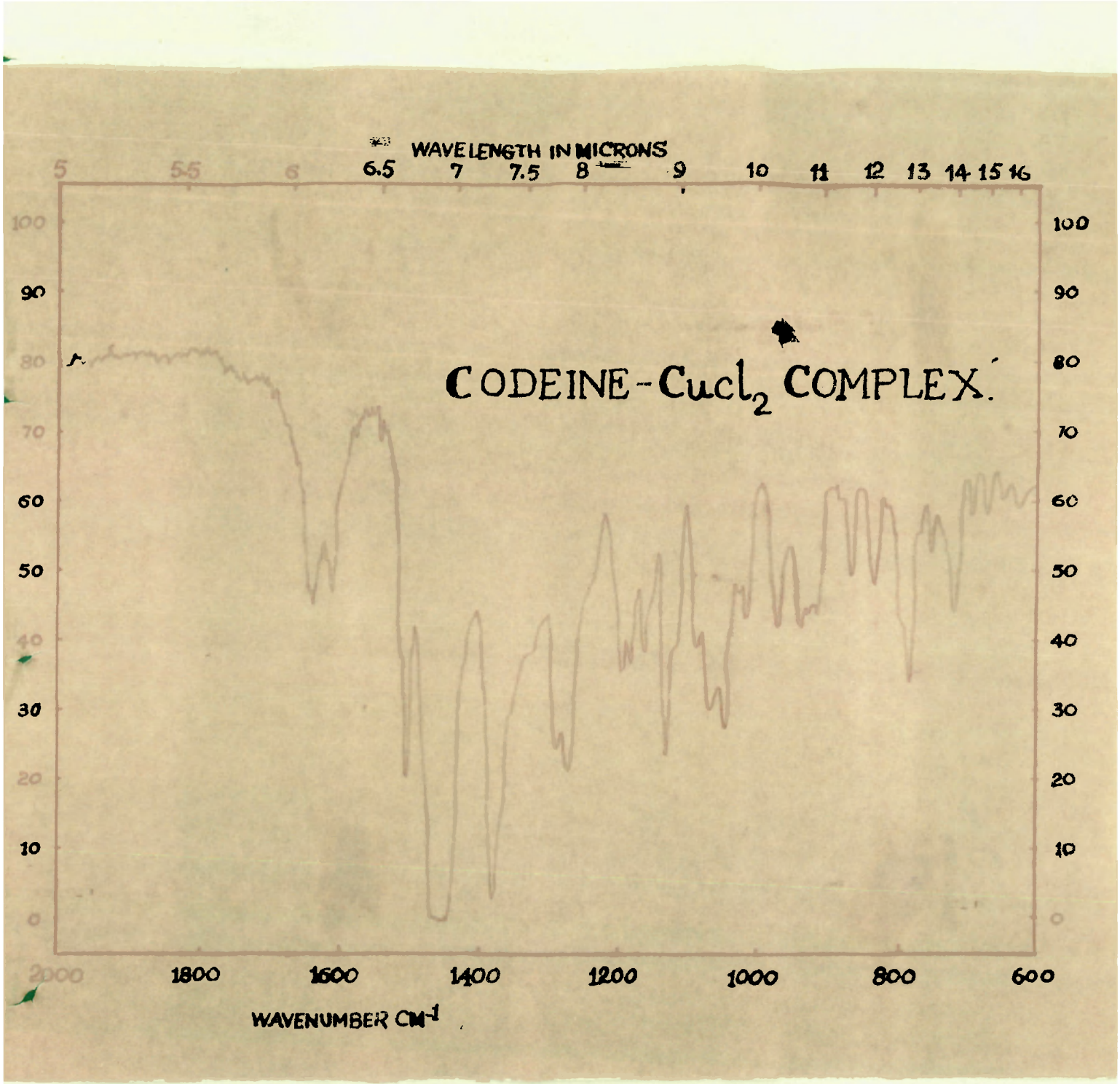

Plate No.11 - I.R. Spectra of Codeine-$CuCl_2$ complex

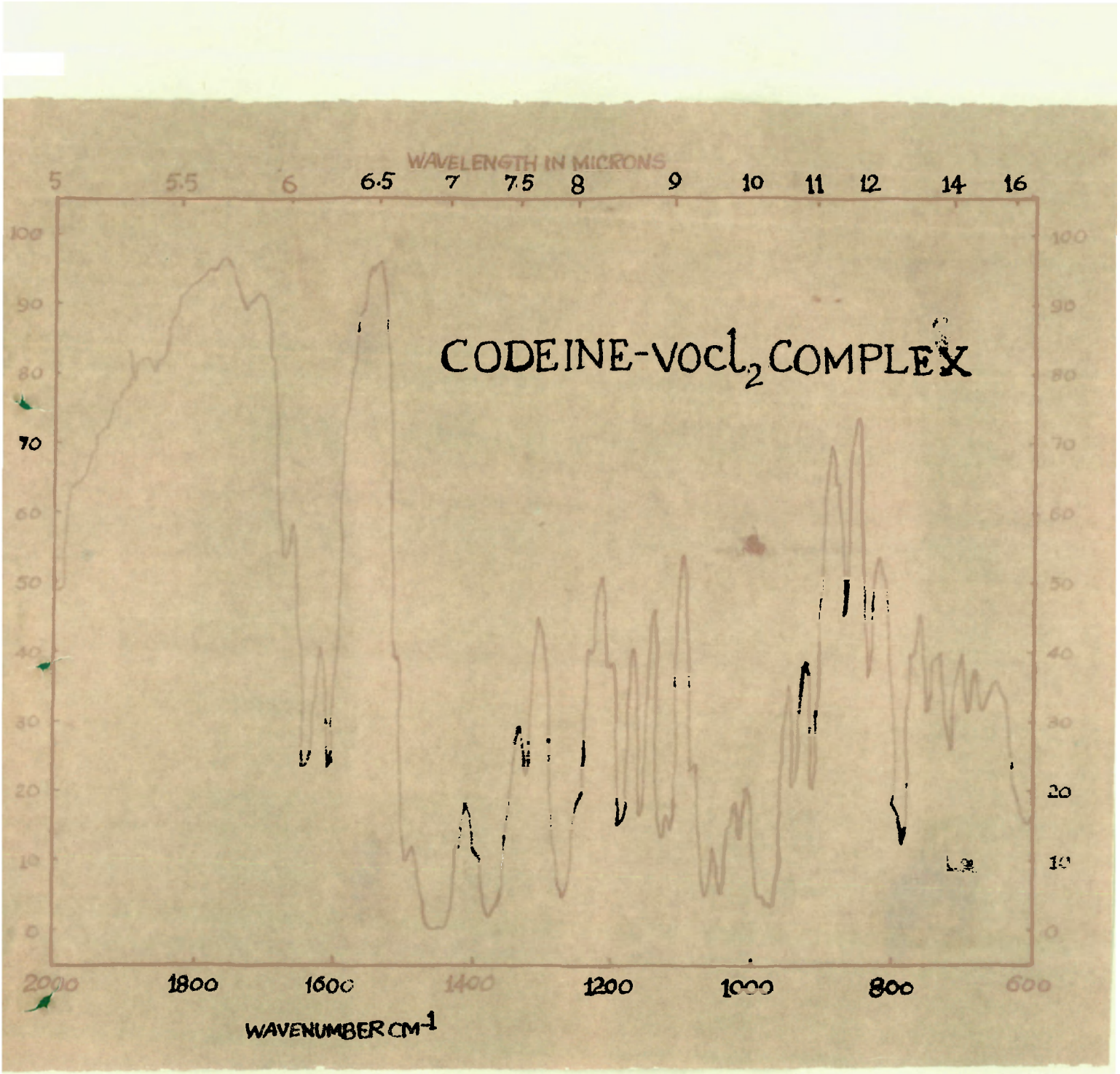

Plate No.12 - I.R. Spectre of Codeine- $VOCl_2$ complex

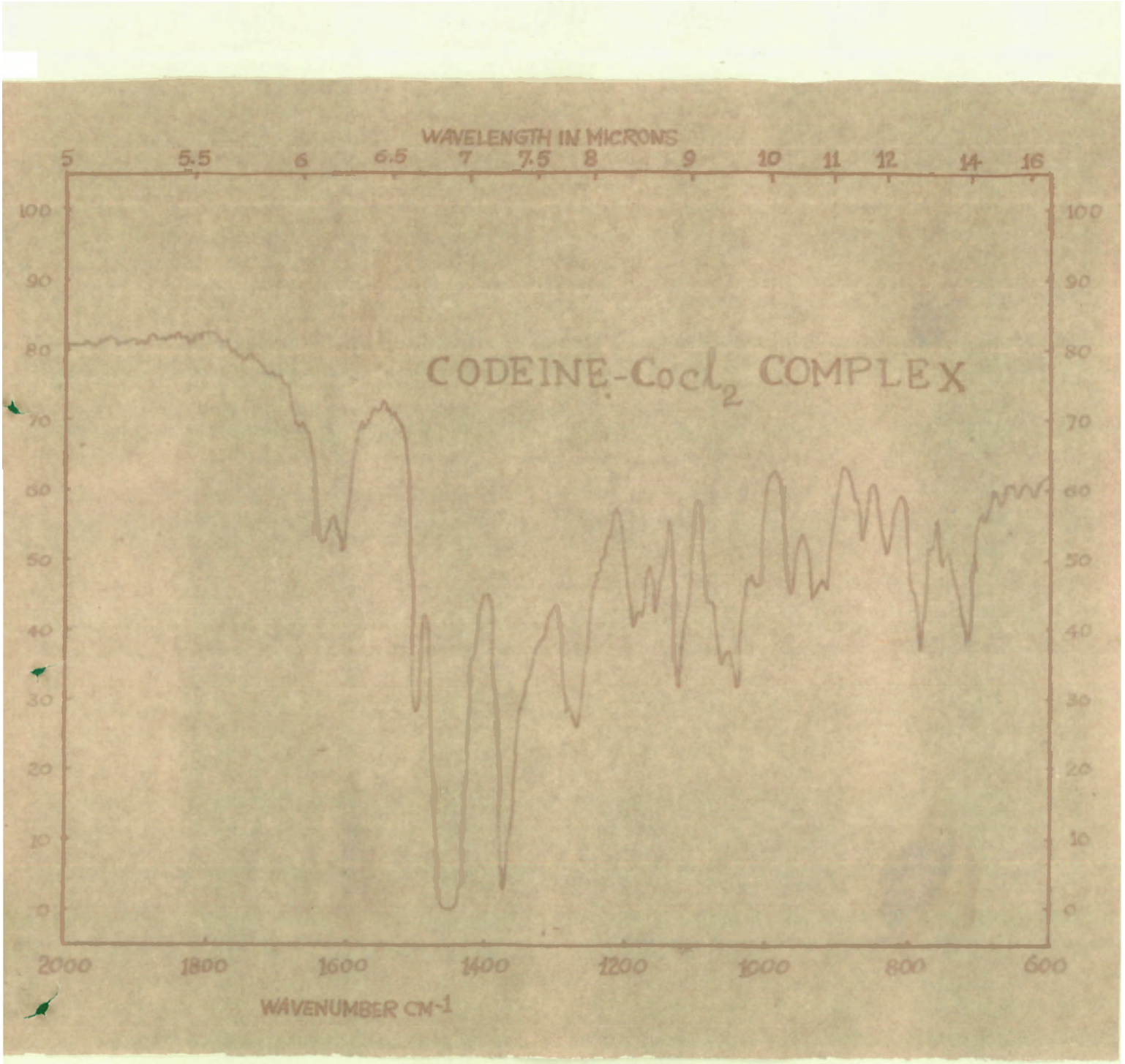

Plate No.13 - I.R. Spectra of Codeine-$COCl_2$ complex

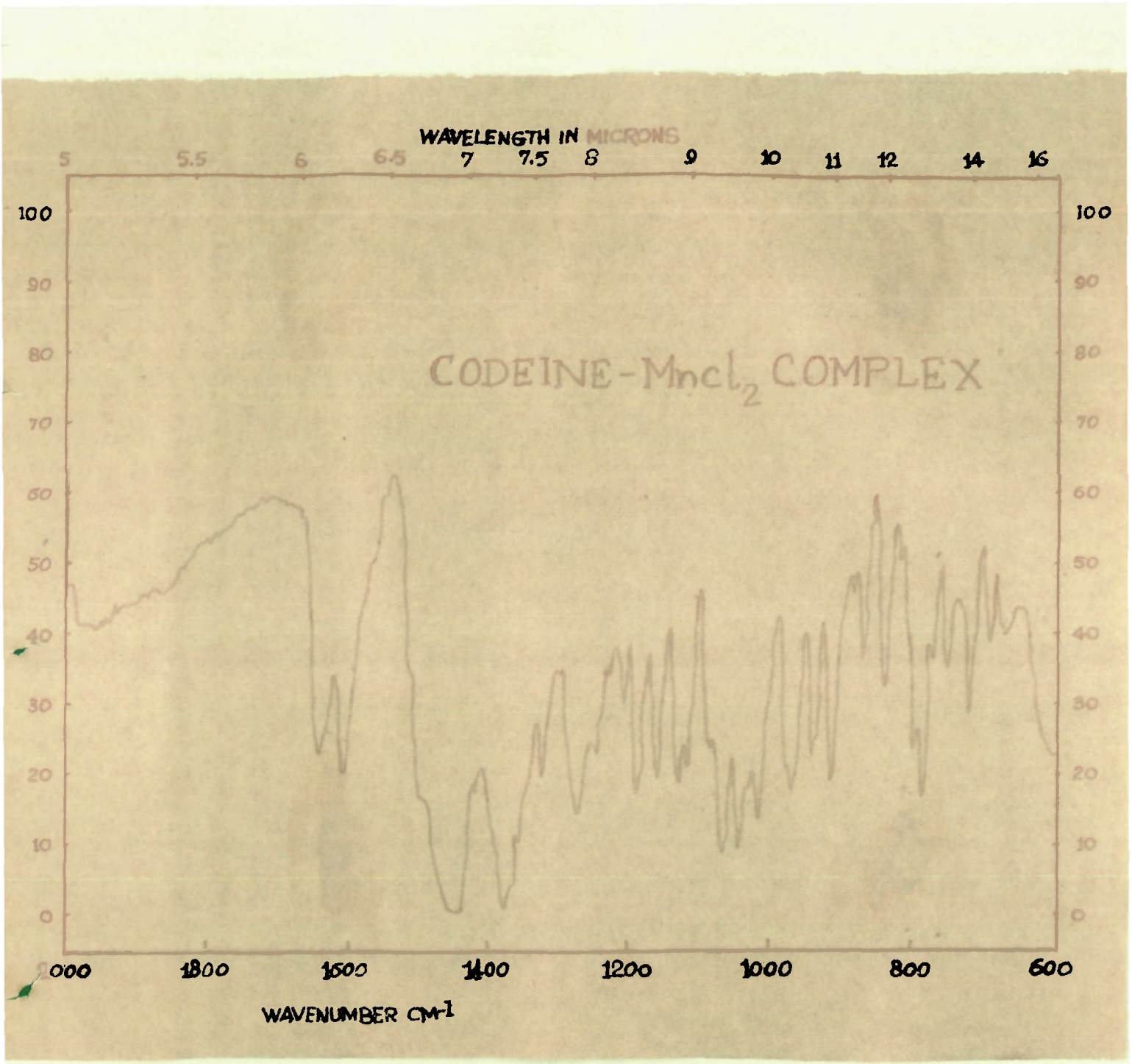

Plate No. 14 - I.R. Spectra of Codeine $MnCl_2$ complex

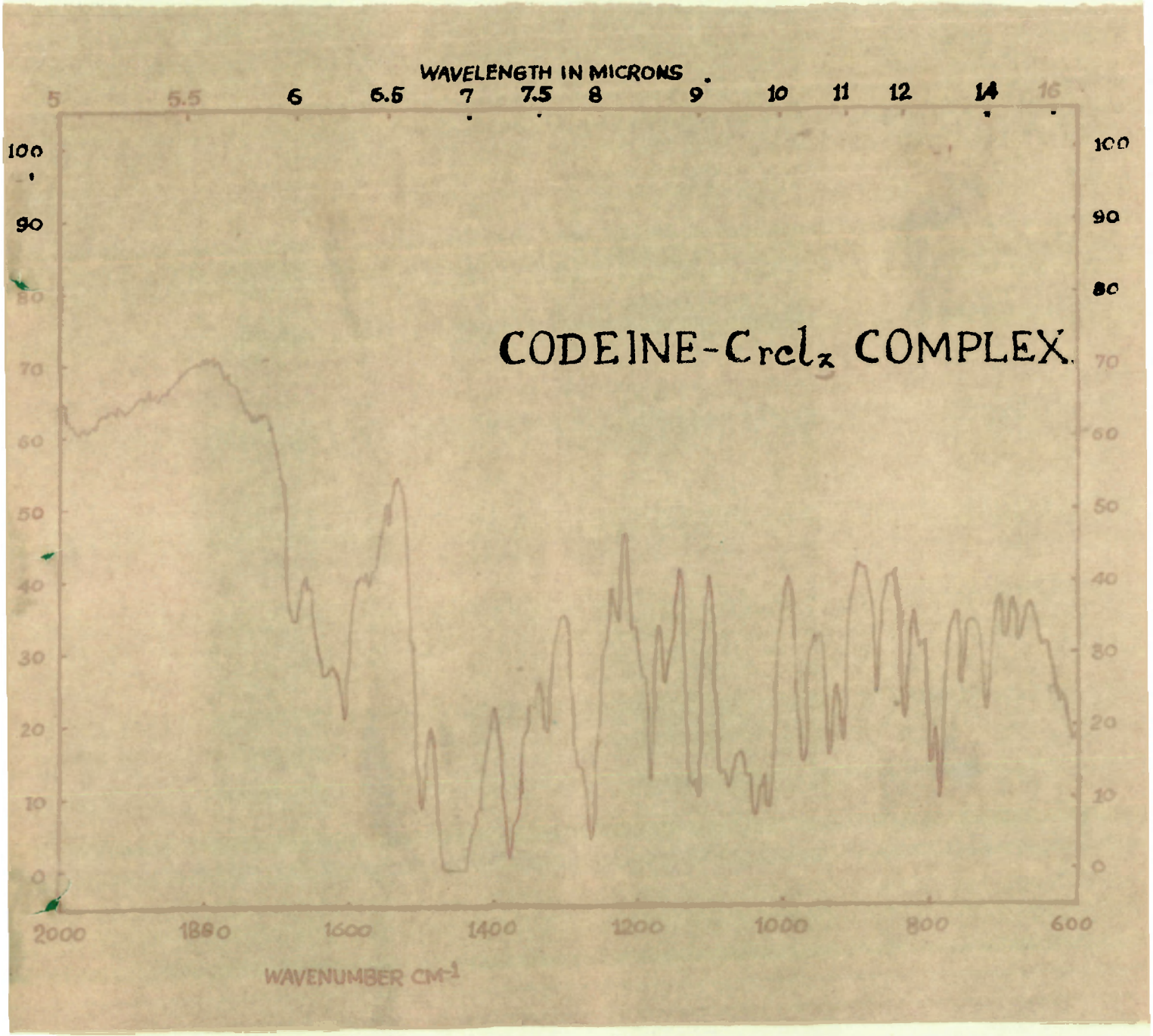

Plate No.15 - I.R. Spectra of Codeine-$CrCl_3$ complex

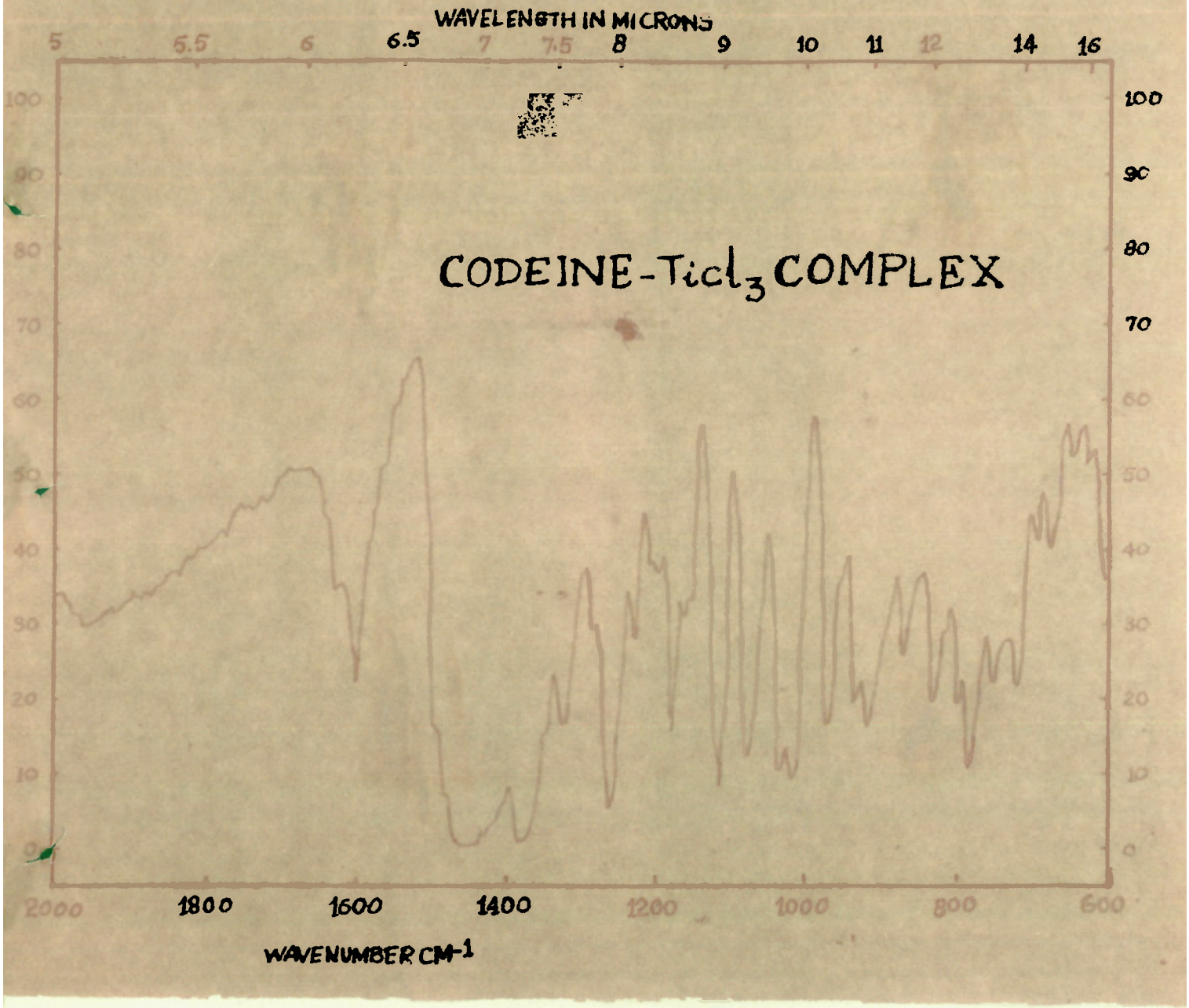

Plate No.16 - I.R. Spectre of Codeine $TiCl_3$ complex

RESULTS AND DISCUSSION

In the present studies, the complexes of alkaloids such as quinaldine, brucine, quinine and codenine with a number of transition metal ions e.g., titanium (III), oxovanadium (IV), oxouranium (VI), nickel (II), copper(II), manganese (II), chromium (III) and cobalt (II) have been synthesised. With quinaldine, there is formation of 2:1 complex (Ligand:Metal), with titanium (III) chloride(yellow), oxovanadium (IV) chloride (grey), oxouranium (VI) sulphate, (dark yellow) and copper (I) chloride (light yellow).

With quinine only 1:1 complexes with oxovanadium(IV) chloride (steel grey) and titanium (III) chloride (mustard) could be isolated in sufficiently pure form. These complexes are soluble in water but insoluble in organic solvents including ethanol. Brucine gives 1:1 products with $VOCl_2$ (grey), $TiCl_3$ (light yellow) and UO_2SO_4 (dark yellow). Like, quinaldine and quinine these are insoluble in organic solvents. With codeine a series of complexes could be isolated with various metal ions namely, Ni^{2+}(light green), Cr^{3+}(light green), Mn^{2+}(pink), VO_2^{2+}(dark grey), Ti^{3+} (dirty yellow), CO^{2+}(bluish green) and Cu^{2+} (mustard). The chemical analysis of these complexes indicate a combining ratio of 1:2 for the metal and the ligand. These complexes

are highly soluble in water, but insoluble in alcohols, acetone, tetrahydrofuran, chloroform etc.

All the products mentioned above have been isolated by using tetrahydrofuran as a crystallising medium. The insolubility of these complexes in organic solvents, but high solubility in water together with the fact that the Cl^- ions present are out side the coordination sphere indicate the non-electrolytic behaviour of these complexes.

The infra red spectra of metal - alkaloid complexes were studied to investigate the nature of coordination. The measurements were made in the region 3 to 16 μ in case of quinaldine, quinine and brucine, however, in codeine complexes the measurements were extended to far infra red region. The information regarding the bonding in these complexes was obtained by comparing the spectra of the complexes with those of the alkaloids and correlating the major changes (or shifts) occurring in the bands assigned to possible coordination sites.

In the proceeding paragraphs details of the spectra of the various alkaloids complexes are described and the correlation obtained by comparing with the spectrum of the respective alkaloid have been discussed.

Quinaldine Complexes

The i.r. spectra of quinaldine and its complexes with titanium(III) chloride, oxovanadium(IV) chloride and oxouranium(VI) sulphate were studied in the region 3 to 15 u. The spectra of the complexes were studied by compering with that of the ligand, and with the assumption that there occurs no major change on coordination with heterocyclic amines. Besides the region ca.3000 cm^{-1} where CH stretching vibrations[10] take place, there are four regions which are important, while considering the spectra of the metal heterocyclic amine complexes. The regions are:

(I) ca.1650-1400 cm^{-1} (CC, CN ring stretching vibrations[11])

(II) ca.1300-1100 cm^{-1} (CH in plane deformation vibrations[12])

(III) ca. 1000 cm^{-1} (ring skeletal vibrations[13])

(IV) ca. 850-700 cm^{-1} (CH out of plane deformation vibration[14])

The positions and intensities of the various bands in the above regions are summarised in the table(No.1).

(a) Titanium(III) chloride-quinaldine complex:

In the complex, the bands at 3000(w) and 2600(v.s) correspond to CH stretching band of quinaldine at 3000cm^{-1}(m). The bands at 1650(v.s), 1590(m), 1500(m), 1410(v.s), 1380(v.s) correspond to ring CC, CN stretching vibration occuring at 1625(s),

1600(v.s), 1570(m), 1500(v.s), 1425(s), 1375(v.s). There are two minor changes occur on coordination,(I) there is reduction in number of bands and (II) there is slight shifting to higher frequencies. The ring skeletal vibrational band occuring at 955 cm^{-1} in the quinaldine is shifted to a higher frequency band at 970 cm^{-1}. The region near 850-700cm^{-1} assigned to CH out of plane deformation modes gave some useful informations regarding the bonding in the complex. There is appreciable shifting of the bands to the higher wave numbers together with increase in intensities, a characteristic of coordinated heterocyclic nitrogen. In quinaldine, the three bands found at 825(m), 790(m), and 750(s) are due to CH out of plane deformation modes, the corresponding bands occur in the complex at 855(m), 850(v.s) and 775(v.s).

(b) Oxovanadium(IV) chloride - quinaldine complex:

The band observed at 2950(m) in the complex is attributed to CH stretching vibrations of heterocyclic ring and corresponds to the medium intensity band found at 3000cm^{-1} in quinaldine. The ring stretching bands obtained at 1625, 1600, 1570, 1425 and 1375 cm^{-1} are shifted to higher wave numbers, these bands are observed in the complex at 1650, 1500, 1450, and 1420 cm^{-1} with higher intensities. There is

splitting of the bands in the region of CH in plane deformation modes on complexation, the four bands observed in the ligand are splitted into eight bands of greater intensities. This behaviour is not so pronounced in case of Ti (III) complex. The ring skeletal vibrations are greatly affected on coordination as is shown by an increase of 30 cm^{-1} from quinaldine to vanadyl-quinaldine complex. This indirectly indicates the strengthening of metal -π nitrogen bond via d_π orbital of the metal. The three bands of medium intensities at 825, 729 and 750 cm^{-1} are shifted to the bands of higher wave numbers (850, 785, 765 cm^{-1}) and with stronger intensities. This behaviour in the region of CH out of plane deformation vibrations is the characteristic of coordinated heterocyclic nitrogen.

(c) Oxouranium(VI) sulphate - quinaldine complex:

The CH stretching vibrations remain unaltered on coordination in uranyl sulphate complex. The ring stretching vibrations are slightly shifted to higher wave numbers in the uranyl complex as observed in the corresponding vanadyl and titanous complexes. There is little change in the position of bands on coordination in the region of CH in plane deformation modes, also the bands are of diminisher intensities. The ring skeletal vibration at 930 cm^{-1} in the uranyl complex indicates the shifting of band towards the

lower frequency side. The behaviour of i.r.spectral bands in the region of CH in plane and ring skeletal vibrations in the uranyl complex is unique in the sense that a some what reverse phenomenon occurred to that exhibited by VO^{2+} and Ti^{3+} complexes. Generally, the coordination in amines results with the shifting of bands of higher wave numbers, splitting of the bands and appearence of intenser bands. The CH out of plane deformation bands are observed in the UO_2^{2+} complex at 830 and 780cm^{-1} indicating the shifting to higher frequencies on coordination. A behaviour which is similer to cooresponding Ti(III) and VO^{2+} complexes.

From the infra red spectral studies of the above mentioned complexes.it may be concluded that $VO^{2+}$and Ti^{3+} complexes show characteristic behaviour typical of coordinated heterocyclic nitrogen e.g., shifting to higher wave number specially in the regions of ring skeletal and CH out of plane deformation vibrations regions. The changes are more pronounced in the vanadyl complex and may be explained in terms of π-bonding by the interaction of vacant d-orbital of the metal with delocalized π-orbitals of the heterocyclic nitrogen. The more marked changes on coordination in the vanadyl complex are indicative of stronger

metal nitrogen bond in the vanadyl complex in comparison to titanous complex. This is perhaps due to the availability of more d electrons in the vanadyl ions and greater affinity of VO^{2+} for heterocyclic nitrogen. Besides absence of distinct changes, the uranyl complex on coordination, particularly in the region near Ca.1300-1100cm^{-1} exhibited a some what opposite behaviour to that observed in the corresponding Ti^{3+} and VO^{2+} complexes. This anomalous behaviour is difficult, to be explained, but most plausible explanation may be the weaker bonding in the uranyl complex.

Quinine Complexes

The infra red spectra of quinine and its complexes with titanium(III) chloride and oxovanadium(IV) chloride were studied in the range 2.5 to 16 u using KBr media.

The quinine alkaloid[2] is a double system consisting of a π deficient substituted heterostomic nucleus(6-methoxy quinoline) and a heteroparaffinic amine (quinuclidine ring). Due to the presence of various functional groups, the complexities in the spectra are expected and are evident by the appearence of numerous bands in the spectra of the alkaloid and of the complexes. Thus it is difficult to give specific assignments to every band, but some of the bands undoubtly be distinguished from the others in the same region due to the definite assignments available in the literature. The positions and intensities of the various bands present in quinine and its complexes are summerised in table No.2.

The OH secondary stretching vibrations[15] appeared at 3650 cm^{-1} in the quinine whereas the corresponding bands in Ti^{3+} and VO^{2+} complexes are at 3560cm^{-1}. The medium intensity bands at 3350, 3200 and 2700cm^{-1} in the quinine are assigned to CH stretching band for quinoline ring,[10] methoxy[16] and vinyl[17] groups, respectively. In the Ti^{3+}

and VO^{2+} complexes, these bands appeared at 3000 and 2400cm^{-1} of the same intensities. The shifts in the frequencies of OH and CH stretching vibrations indicate coordination of the quinine ligand with the metal.

The ring CC, CN stretching vibrations of substituted quinoline appeared in the form of strong bands[11] at 1640, 1500(sh) and 1475 cm^{-1}. In the complex, Ti^{3+}- quinine, the bands in this region appeared at 1635, 1610, 1555, 1500 cm^{-1} and 1450 cm^{-1}, and corresponding bands in VO^{2+} complex at 1635, 1610, 1550 and 1460 cm^{-1}. The shifting of the bands to the higher frequency side and increase in the number of bands on complexation in this region is an indirect indication of coordination through heterocyclic nitrogen.

A number of bands appeared in the spectrum of quinine in the region ca.1000-1100 cm^{-1}. Out of these bands, the medium intensity band at 1040 cm^{-1} is assigned to CN stretching modes of quinuclidine ring[18], there is shifting of this band to lower frequency side on coordination e.g., Ti^{3+} (1010cm^{-1}) and VO^{2+}(1020cm^{-1}). The strong band at 1090cm^{-1} in the quinine is a C-OH stretching band, this band remains almost unaltered on coordination as is evident from the appearence of this band at 1100 cm^{-1} in the Ti^{3+} complex, and at 1095cm^{-1} in the VO^{2+} complex. The strong

band at 1200cm^{-1} in the spectrum of the ligand and 1170cm^{-1}(m) in the complexes is ascribed to -CO stretching vibrations of methoxy group.[16]

The several bands in the region ca.900-1000cm^{-1} result from ring skeletal vibrations of heterocyclic aromatic ring and CH out of plane deformation vibrations of quinine.[19] The 1025cm^{-1} band is undoubtfully arising from ring skeletal modes, and the complexes give corresponding bands at 990cm^{-1} (Ti^{3+}) and 1025 and 920cm^{-1}(VO^{2+}). The medium intensity bands at 880, 855, 835 and 715 cm^{-1}, are CH out of plane deformation vibrations of the rings present in the quinine. Out of these bands at least two bands at high frequencies e.g., 880 and 855cm^{-1} belong to paraffinic ring system and the last two belonging to aromatic heterocyclic ring system. In the quinine- Ti(III) chloride complex, the CH out of plane deformation vibrations appeared at 850, 760 and 715cm^{-1}, whereas corresponding bands in vanadyl complex at 850,810 and 720cm^{-1}. This indicates reduction in the number of bands but shifting to higher frequencies. The appreciable changes in the region of CH out of plane deformations indicate coordination of metal through heterocyclic nitrogen.

The evidence regarding the nature of coordination in Ti^{3+} and VO^{2+} complexes may be inferred from the i.r.studies by considering the spectral domains largely effected on

coordination. The ring CC, CN stretching vibrations of substituted quinoline ring are largely influenced on coordination as is exhibited by the increase of the number of bands and shifting to higher frequencies, a characteristic of coordinated aromatic heterocyclic nitrogen. This is further evident by the changes in the regions of CH of plane and CH in plane vibrations. Considering the possibility of coordination through nitrogen of quinuclidine ring; the reactivity of quinuclidine ring system arises due to high base strength and the ready availability of the nitrogen electron pair through reduced F-strain[20] may invite the possibility of coordination through this nitrogen, but there is only one evidence in favour of this formulation viz., shifting of the CN band (assigned at 1040cm^{-1} in quinine) to lower frequency on coordination. However, there are more evidences in favour of coordination through less basic nitrogen of π-deficient heteroatomic nucleus of the substituted quinoline. The substituted groups, OH and methoxy in the ring, and vinyl group in the paraffinic ring do not seem to play any role in the complex formation.

From the analysis of the infra red spectral data of quinine and its complexes, there is convincing information of coordination through heterocyclic nitrogen. Moreover, the results are not conclusive, but there are more evidences

for the part played by aromatic heterocyclic nitrogen in coordination.

Brucine Complexes

The infra red spectra of brucine and its complexes with oxovanadium(IV) chloride, titanium(III) chloride and oxouranium(VI) sulphate were studied in the region 2.5 to 15 u using KBr phase.

Brucine is complex indole alkaloid and due to the presence of several ring systems viz., pyrrocoline ring, tetrahydroindole, keto-piperazine and 1-oxa-$\triangle$-3-cycloheptene rings together with various functional groups such as OCH_3, -N-CO, CH-$\overset{CH_2}{N}$ CH_2 etc., the spectrum of the alkaloid consists of a large number of bands of variable intensities. Like other alkaloids it is not possible to give specific assignments to all these bands, however, the characteristic bands arising from certain familiar groups may easily be singled out from the others. The assignments to the various bands are given in table No.3. There are three important coordination sites in the alkaloid namely,-N-CO, the acylazole group, the oxygen of the 7-membered oxepine ring and the tertiary nitrogen CH_2-$\overset{CH_2}{N}$-CH_2 present in the 5/6 pyrrocoline ring.

The carbonyl stretching and CN, stretching modes of n-acylazole system[21] belonging to keto-piperazine occurred at 1626 and 1335cm^{-1}, respectively, in brucine. The 1665cm^{-1} strong band is assigned to C=C stretching vibrations. On coordination, the bands arised from C=O stretching and CN stretching are disappeared as is indicated by the absence of these bands in the spectra of the complexes. The 1665cm^{-1} band, however, remains almost unaltered on coordination. The strong band at 1450cm^{-1} in the ligand is assigned to CC, CO stretching vibrations of the oxepine ring.[22] The spectra of the complexes indicate non shifting of these bands and appeared at the same positions. The band at 1090cm^{-1} in the alkaloid appears in the form of a shoulder is assigned to CN stretching of the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring.[18] The band is shifted slightly by 5 to 10 cm^{-1} to the lower frequency side on coordination.

With the available information from the study of the infra red spectra of the brucine and its complexes with $VOCl_2$, $TiCl_3$ and UO_2SO_4, it may be concluded that the coordination takes place through nitrogen of acylazole system as indicated by the disappearence of 1335cm^{-1} band assigned to CN stretching vibrations, appeared at 1626cm^{-1} in the alkaloid. The position of the other bands arising from the groups other than that of acylazole considered as

possible coordination sites did not show any change on coordination viz., oxygen of 1-oxa- Δ-3-cycloheptane (oxepine) and tertiary nitrogen of the pyrrocoline rings. Similarly the band assigned to CH stretching ($3000cm^{-1}$), $-OCH_3$ stretching ($1200cm^{-1}$) and C=C stretching[23] ($1665cm^{-1}$) remain almost unaltered on coordination.

Codeine complexes

The medium intensity band at $3600cm^{-1}$ present in the codeine is the secondary OH stretching band[15], however, in the complexes no band is observed at this frequency. For example, Cu^{2+}, CO^{2+} and Ni^{2+} only show the corresponding bands at 3460 cm^{-1}, $3560cm^{-1}$(sh) and $3530cm^{-1}$ in the spectra, and Mn^{2+}, Ti^{3+}, Cr^{3+} and oxovanadium(IV) chloride, however, do not give any band in the region ca.$3500-3600cm^{-1}$. A number of high absorption bands usually broad of variable intensities appeared in the region ca.$3000-3400cm^{-1}$ and are assigned to CH stretching vibrations of various functional groups present in the codeine.[10] The position of bands remains almost constant in the complexes. The shifting of the OH stretching band to the lower wave number in nickel(II) cobalt (II) and copper(II) complexes, and the total absence of any band in case of Mn^{2+}, Ti^{3+}, Cr^{3+} and VO^{2+} is clearly an evidence of coordination through hydroxyl group. The

positions and intensities of the various bands present in codeine and its complexes are summerised in the table No.4.

The CH_3-N stretching modes[24] are found to occur in the region ca.2820-2700 cm^{-1}. The spectrum of codeine shows a weak band at 2710cm^{-1} in this region whereas in the complexes of Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, Ti^{3+}, Mn^{2+} and Cr^{3+}, the corresponding bands appeared at 2730cm^{-1}, 2710cm^{-1}, 2720cm^{-1}, 2735cm^{-1} and 2720cm^{-1}, respectively. The almost unaltered positions of CH_3N stretching band indicates that there occurs no major change on coordination.

The strong band at 1630cm^{-1} in the codeine is assigned to C=C stretching vibrations.[15] The position of this band remains the same in the spectra of the complexes. The bands at 1605cm^{-1}, 1265cm^{-1} and 970cm^{-1} are assigned to ring stretching, CH in plane and ring skeletal vibrations, respectively, of dihydro substituted furan ring.[25] There are only minor shifts in the band positions in the spectra of the complexes. The CN stretching vibrations[18] of tertiary nitrogen present in the 6-member saturated ring occurs at 1045cm^{-1} in the ligand and almost at the same positions in the complexes. The band at 1090cm^{-1} appeared in the form of a shoulder in the codeine may be assigned to C-OH stretching vibrations[26], the band is slightly lowered by

5 to 10 cm^{-1} in the complexes. The methoxy stretching vibrations occurring at 1190cm^{-1} in the ligand are found to occur at almost same numbers in the complexes.

In the far infra red region the bands at 310-230cm^{-1} occurring in the spectra of the complexes is absent in the ligand and this band is assigned to metal- chloride stretching vibrations.[35]

In the present studies on the interaction of transition metal ions with alkaloids namely, quinaldine, quinine,brucine and codeine, the information regarding the bonding in the complexes has been obtained entirely on the basis of interpretations of the infra red spectra of the alkaloids and their complexes. The results of these studies can be summerised as follows.

(I) In quinaldine complexes, the coordination takes place through heterocyclic nitrogen of the quinoline as is evident from the chenges taking place in the regions of CC, CN ring stretching vibrations, ring skeletal vibrations and CH out of plane deformation vibrations.

(II) The coordination in quinine complexes is most probably taken place through heterocyclic nitrogen of quinoline, as there are more evidences in favour of the latter than the more basic nitrogen of the quinuclidien ring. The evidences

regarding the coordination through nitrogen of π-deficient quinoline is largely based upon the changes in CC, CN ring stretching, CH out of plane vibrations of quinoline ring.

(III) In brucine complexes, there are convincing evidences regarding the coordination through nitrogen of acylazole system as is evident by the disappearence of the frequencies at 1626cm^{-1} and 1335cm^{-1} assigned to C=O stretching and CH stretching vibrations of keto-piperazine ring.

(IV) In codeine complexes the coordination takes place through secondary hydroxyl group present in the alkaloid and there is little evidence regarding the coordination through tertiary nitrogen or oxygen of furan ring.

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R E S U M E

1. Studies on the complexes of aminoacids with chromium(II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(VI) sulphate:

The complex formation between Cr^{2+}, Ti^{3+}, VO^{2+} and UO_2^{2+} with various aminoacids has been studied in solution. The composition of the complex species formed in solution was determined by potentiometry and conductometry. With chromium (II) chloride both sulphur containing aminoacids viz., cysteine, taurine and methionine, and non sulphur containing aminoacids such as glycine, DL-α-alanine, β-alanine, DL-serine, DL-valine, L-proline, DL-leucine and L-asparagine were used. With other metal ions only non sulphur containing aminoacids were employed. A combining ratio of 1:1 for the metal and aminoacids was obtained in each of the complexes.

The stability constants of the aminoacid complexes were determined by conducting pH-metric titrations. The titrations were performed by employing mixtures containing (a) aminoacid (b) metal and (c) aminoacid + metal, using standard KOH as a titrant. The formation constants of the complex species were calculated applying Bjerrum's method simplified by Albert for aminoacid system. By titrating

each aminoacid in the presence of various metallic ions, the pH-values were obtained after each addition of alkali. The values of [Sc] , the concentration of free aminoacid and $\bar{n}$ the average number of molecules of aminoacid bound by one atom of the metal were determined from the equations(IV) and (V) (Chapter I, page,153).

The formation curves (plots of $\bar{n}$ versus -log [Sc])are given in figures 2C to 35C in chapter I. From these curves the values of -log [Sc] were evaluated at $\bar{n} = 1$ and subsequently the values of log K_s by applying the relation, log K_s = -2log [Sc] (Chapter I, page,154). The calculated values of log K_s were determined by the addition of average values of log K' and log K". The values of overall stability constant, log K_s obtained from the formation curves were found to be in good agreement with those calculated (table No.36, Chapter I).

Various qualitative correlations may be obtained from the study of log K_s values (summerised in the table No.36, Chapter I) and comparing them with pK_a's values of the corresponding aminoacids. The order of stabilities of aminoacid complexes can be classified into three categories namely, (I) aminoacid complexes containing β-alanine, DL-α-alanine and L-proline, where the order of stability is:

$UO_2^{2+} \approx Cr^{2+} > Ti^{3+} > VO^{2+}$; (II) L-asparagine and DL-serine complexes where metals follow the order: $Ti^{3+} > Cr^{2+} \approx VO^{2+} > UO_2^{2+}$ and (III) in which metals fall in between the groups(I) and (II) e.g., VO^{2+} Cr^{2+} UO_2^{2+} Ti^{3+} and includes the aminoacids, L-leucine and DL-valine. The aminoacids belonging to the first category have highest pK_a's values e.g., L-proline (10.68), β-alanine (10.66) and DL-α-alanine (9.97) whereas the two aminoacids, L-asparagine and DL-serine belonging to second category have the lowest pK_a's values. The rest of the aminoacids have pK_a's values in between (I) and (II).

The order of stability constants in the metal complexes, in general, is: L-proline > β-alanine > DL-α-alanine > glycine > L-leucine > DL-valine > DL-serine > L-asparagine, which is roughly the same as that of the pK_a's order of the aminoacids e.g., L-proline (10.68), the highest and L-asparagine the lowest (8.85).

In case of Cr^{2+} complexes with sulphur containing aminoacids, the order of stability constants is: Cysteine > methionine > taurine (table No.36, Chapter I), which runs parallel to the order of pK_a's values of cysteine (10.28), methionine (9.34) and taurine (9.08). By comparing the log K' and log K_s values of cysteine complex with those of

corresponding glycine and DL-α-alanine complexes, the higher stability of cysteine complex is attributed to the involvement of sulphur in coordination. This view is further strengthened by the fact that besides - NH_2 and COO^- groups, the log K' and log K_s values of taurine were much lower than that for cysteine. On the basis of these comparisons, the coordination through COO^-, NH_2 and -S- has been suggested in the cysteine complex. In Cr^{2+} - methionine complex, only two coordination sites viz., COO^- and $-NH_2$ are involved as may be concluded on the basis of similar comparisons.

CONCLUSION:-

Chromium (II) chloride, titanium(III) chloride, oxovanadium(IV) sulphate and oxouranium(VI) sulphate form (1:1) complexes with aminoacids namely, glycine, L-asparagine, DL-valine, DL-serine, DL-proline, DL-leucine, L-leucine, DL-methionine, cysteine and taurine. The stability of aminoacid complexes increases with increase in pK_a's values viz., L-proline being the highest and L-asparagine the lowest. Uranyl complexes have the highest log K_s values for the aminoacids with largest dissociation constants e.g., β-alanine, DL-α-alanine and L-proline against Ti^{3+}complexes haveing highest log K_s values with aminoacids of lowest

dissociation constants e.g., L-asparagine and DL-serine. Cr^{2+} and VO^{2+} complexes have almost the same stabilities and give highest values with aminoacids having pK_a's value in the middle of the aminoacid series. In general, the stability of the aminoacid complexes decreases with increase in the chain length of the carbon atoms and the distance between amino and carboxylic groups. The coordination in the Cr^{2+}- cysteine complex takes place through COO^-, $-NH_2$ and -SH groups, whereas in the methionine complex it occurs only through $-NH_2$ and COO^- groups.

2. Behaviour of Copper(I) iodide in aqueous potassium iodide containing aminoacids:

Evidence for the complex formation between insoluble copper(I) ion and aminoacids has been obtained on the basis of solubility studies. The studies consist of the determination of copper(I) in two sets of solution, the one without and the other with aminoacid. From the solubility data, there is an appreciable difference in Cu^+ contents of the two sets (table 2A, 2B and 2C, Chapter II). This is an indirect evidence for the complex formation in the aminoacid system consisting of Cu_2I_2, KI and aminoacid in aqueous medium.

The concentration of Cu_2I_2 combined with aminoacid was determined by substracting the concentration of Cu_2I_2 in

aqueous potassium iodide without aminoacid from that of Cu_2I_2 with the same concentration of KI but in the presence of aminoacid. The concentration of aminoacid consumed in complex formation was calculated by the difference of the concentration of aminoacid added initially and that of estimated from the Cu_2I_2 solution colorimetrically.

From the solubility data there is evidence for the formation of 1:1 complex species with L-leucine and L-proline, and 1:2 complex in case of glycine. The coordination in 1:1 species occur through amino and carboxylic groups with the subsequent replacement of one proton from the latter. In 1:2 complex the mechanism consists of the formation of 1:1 complex with copper(I) in the initial stage and subsequent formation of 1:2 chelate due to the oxidation of copper(I) to copper(II).

The plot of free aminoacid concentration [L] and Ksp, the solubility product of the aminoacid complex gives straight lines with slopes of 1:1 for L-leucine and L-proline, and 1:2 for glycine supporting thereby the results of solubility measurements (figure No.2, Chapter II).

Conclusion:

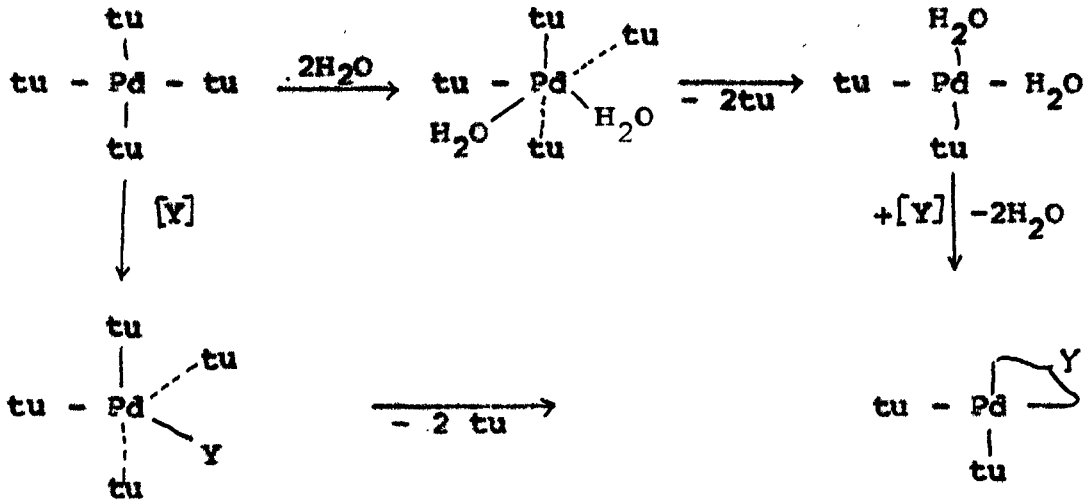
The composition of the complexes formed by the interaction of copper(I) and aminoacid has been determined

on the basis of solubility measurements. The concentration of copper(I) varies significantly when aminoacid is added to the solution of Cu_2I_2 in aqueous potassium iodide. The difference in copper(I) contents gives the actual concentration of copper(I) combined with aminoacid in complex formation. A ratio of 1:1 is obtained for L-leucine and L-proline complexes and 1:2 for glycine complex. From the slopes of the linear plots of solubility product of aminoacid complex, Ksp and [L] ; the free aminoacid concentration, same combining ratios for metal aminoacid complexes are obtained, thus confirming the results of solubility measurements.

3. Substitution reactions of square planar tetra Kis (thiourea) palladium(II) chloride with some aminoacids:

The kinetic of the substitution reactions of square planar tetra kis (thiourea) palladium(II) chloride, $Pd(tu)_4Cl_2$ with various aminoacids viz., glycine, DL-α-alanine, threonine, L-asparagine, DL-valine, DL-serine and L-proline have been studied by spectrophotometric method. The studies showed that these reactions proceed by a displacement mechanism following a two term rate law. The applicability of two term rate law in the substitution reaction of Pd(II) complexes is demonstrated by the linear plots obtained by

plotting $K_{obsd.}$, the first order rate constant determined experimentally versus [Y], the concentration of aminoacid (figure No.8, Chapter III). The values of K_1 and K_2, the first and second order rate constants, respectively, were determined from the intercepts and slopes of the linear plots (table No.8., Chapter III). Following Basolo, the rate constant K_1 represents the slow displacement of thiourea molecule by the solvent H_2O which is then readily displaced by the aminoacid. A direct nucleophilic displacement of thiourea by aminoacid is responsible for K_2. The mechanistic path for such type of substitution reaction may be represented as



As a typical example, the $K_{obsd.}$ values at 35°C for the various aminoacids of 0.1M concentrations follow the order: glycine (8.625) > DL-valine (5.75) > DL-serine(4.876)>

L-proline (4.10) > DL-threonine (3.63) > DL-∝-alanine(3.03) > L-asparagine (2.99). The order of increasing ionization constants of ∝-amino carboxylic group is: DL-valine > glycine > DL-serine > threonine > L-asparagine > L-proline. A comparison of the two series indicate the increase in $K_{obsd.}$ values with increase in ionization constants of ∝-amino carboxylic group and consequently the influence of ionization constant on the extent of substitution of aminoacid in the complex.

Conclusion: The mechanism of substitution reactions of square planar $Pd(tu)_4Cl_2$ with various aminoacids have been investigated, spectrophotometrically. The kinetics found to follow the two term rate law expressed as $K_{obsd.} = K_1 + K_2[Y]$ where $K_{obsd.}$ is the first order rate constant determined experimentally, and K_1, and K_2 from the intercept and slope of the linear plots of $K_{obsd.}$ versus [Y]. K_1 represents the slow displecement of thiourea molecule by the aminoacid whereas K_2 is responsible for the direct nucleophilic displacement of thiourea by aminoacid. The influence of ionization of carboxylic group on the extent of substitution of aminoacid in the complex, $Pd(tu)_4Cl_2$ is obvious on comparing the order of $K_{obsd.}$ values for various aminoacid complexes and the corresponding ionization constant values for each aminoacid. With the exceptions of DL-∝-alanine and L-proline, there is an increase in $K_{obsd.}$ values of

aminoacid complexes with an increase in the ionization constant of the corresponding ∝-aminocarbonylic group in the aminoacid series.

4. Metal complexes of alkaloids:

The complexes of alkaloids with some transition metal ions such as Ti^{3+}, VO^{2+}, UO_2^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+} and Cr^{3+} have been synthesised. The complexes with codeine were synthesised with a large group of metal ions namely VO^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Ti^{3+} and Cr^{3+}. Unlike alkaloids, their complexes are in general, highly soluble in water but insoluble in common organic solvents such as alcohol, acetone, ether, chloroform, tetrahydrofuran etc.The results of chemical analyses indicate a ratio of 1:2 (metal:ligand) for quinaldine and codeine complexes, and 1:1 for brucine and quinine complexes.

Infra red spectra of the complexes were studied in order to determine the possible coordination sites in the metal-alkaloid complexes. Useful informations were obtained regarding the nature of coordination on comparing the spectra of the complexes with those of the respective alkaloids and correlating the major changes or shifts occurring in the bands assigned to donor groups pertinent to coordination.

Due to the presence of various functional groups, spectra of the alkaloids consist of numerous bands and it is a remote possibility to give specific assignments to every band. But some of them may be definitely assigned on the basis of spectral data available in literature.

The infra red spectra of quinaldine and its complexes with $TiCl_3$, $VOCl_2$ and UO_2SO_4 give some useful information regarding the bonding in these complexes. The main information is obtained from the changes occurring in the regions Ca.1000 Cm^{-1} and 850 - 700 cm^{-1} assigned to the ring skeletal and CH out of plane deformation vibrations, respectively. The bands arising from ring skeletal vibrations and those from CH out of plane deformation modes are shifted to higher wave numbers together with increase in intensities (table 1, Chapter IV). The changes in the above mentioned regions are more pronounced in the VO^{2+} complex and may be explained in terms of π-bonding through vacant d orbital of the metal, and delocalized π-orbital of the heterocyclic nitrogen. The Ti^{3+} complex also shows similar changes, but to a lesser extent. However, in the UO_2^{2+}-quinaldine complex the changes are least pronounced.

On the basis of the changes in the spectra of quinaldine complexes, the coordination through heterocyclic

nitrogen is inferred, although the bond strength decreases from VO^{2+} to UO_2^{2+}.

In quinine alkaloid, there are three pertinent coordination sites namely, the nitrogen atoms of 6-methoxyquinoline and quinuclidine rings, and a secondry hydroxyl group. The infra red spectra of Ti^{3+} and VO^{2+} complexes give some definite information regarding the bonding in these complexes at one of the possible sites.

The secondary hydroxyl stretching vibrations appeared at 3650cm^{-1} in the quinine alkaloid are shifted to lower frequencies on coordination and the CH stretching vibrations appearing near 3000 cm^{-1} show the same behaviour. A possible consequence from the shifts in OH and CH stretching vibrations is the involvement of heteroatomic nuclues of the substituted quinoline in coordination. Further evidence in favour of coordination through heterocyclic nitrogen is obtained on considering the changes occurring in the regions of ring CC, CN stretching vibrations of 6-methoxy quinoline, ring skeletal vibrations of heterocyclic aromatic ring and CH out of plane vibrations. The bands in these regions are usually shifted to higher frequency side with an increase in the number of bands.

There is not much evidence for the coordination through nitrogen of quinuclidine ring in the complexes of quinine.

The spectrum of the quinine shows a medium intensity band at 1040 cm^{-1} and is assigned to CN stretching modes of heteroparaffinic ring. This band shifts to lower frequency side in the spectra of the complexes viz., Ti^{3+} (1010 cm^{-1}) and VO^{2+}(1020 cm^{-1}). Besides the slight shifts in CN stretching modes, there is a paucity of information in favour of the coordination through more basic and reactive nitrogen of quinuclidine ring.

Brucine is a complex alkaloid belonging to indole group, containing several ring systems, e.g., pyrrocoline, tetrahydroindole, keto-piperazine and 1-oxa Δ-3-cycloheptane together with various functional groups such as CH_3O, -NCO, $CH_2 - \overset{CH_2}{\underset{|}{N}} - CH_2$ etc. The infra red spectral studies were carried out to ascertain the possible coordination sites in the complexes of brucine with $VOCl_2$, $TiCl_3$ and UO_2SO_4.

In the alkaloid, brucine, there are three positions susceptible to coordination namely, -NCO, acylazole group, the oxygen of a 7-membered oxepine ring and the tertiary nitrogen of $CH_2 - \overset{CH_2}{\underset{|}{N}} - CH_2$ present in the 5/6 pyrrocoline ring. In the spectrum of brucine, the CO and CN stretching modes of n-acylazole group, belonging to keto-piperazine ring system occurred at 1626 cm^{-1} and 1335 cm^{-1}, respectively. However, no such bands appeared at these positions in the

complexes. The bands arising from CC, CO stretching vibrations of the oxepine ring, and CN stretching of the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring, appeared at 1450 cm^{-1} and 1090 cm^{-1}, do not show any shift on coordination. Summerising the available information from the infra red spectra of the brucine and its complexes, there is ample evidence for the coordination through nitrogen of acylazole group.

The infra red spectra of codeine and its complexes with Cu^{2+}, CO^{2+}, Ni^{2+}, VO^{2+}, Mn^{2+}, Ti^{3+} and Cr^{3+} give some reliable information regarding the bonding in these complexes. There are three possible coordination sites in the codeine namely, the secondary/hydroxyl group, tertiary nitrogen attached to methyl group and the oxygen of the furan ring.

The medium intensity band at 3600 cm^{-1} in the spectrum of the codeine is assigned to secondary OH group stretching vibrations. However, in the complexes no such band appeared at this frequency. In the Ni^{2+}, CO^{2+} and Cu^{2+} complexes, this band is shifted to much lower frequency whereas in the spectra of Mn^{2+}, VO^{2+}, Ti^{3+} and Cr^{3+} complexes, there is no band in the region Ca.3500-3600 cm^{-1} or in the vicinity. The absence of the bands at this frequency e.g., 3600 cm^{-1} or in the neighbouring region is a clear indication of the coordination of the metal through hydroxyl group. The band

at 2710 cm^{-1} arising from $N-CH_3$ stretching in the codeine and those from ring CC, CO stretching, CH in and out of plane, and ring skeletal vibrations of dihydrofuren ring system remain almost unaltered in the complex (table No.4, page.235). This clearly indicates the very remote possibility of coordination through these two coordination sites viz., $-NCH_3$ and oxygen of the dihydrofuran ring.

Conclusion:

The main evidence in favour of the coordination through heterocyclic nitrogen in the quinaldine complexes with Ti^{3+}, VO^{2+} and UO_2^{2+} is the exhibition of some marked changes usually associated with the spectra of coordinated heterocyclic amines e.g., shifting of the bands to the higher wave numbers together with increase in their numbers. In quinaldine this phenomenon is specially observed in the regions of ring CC, CN stretching vibration (Ca. 1600 cm^{-1}) and CH out of plane deformations (Ca .800 cm^{-1}).

On the basis of studies on the infra red spectra of Ti^{3+} and VO^{2+} complexes with quinine, there is a sufficient evidence for coordination through the heterocyclic nitrogen of 6-methoxyquinoline. This conclusion is derived on the basis of the observed shifts to higher frequencies in the regions of ring CC, CN stretching, ring skeletal and CH out of plane vibrations of substituted quinoline ring on

coordination together with increase in the number of bands. Although the nitrogen of the quinuclidine ring is more basic and electrons are readily available due to reduced"F-strain," but there is little evidence of coordination as indicated by the infra red spectra of the complexes.

The possibility of coordination in brucine arises due to the presence of three important donor groups e.g., -NCO group, a part of keto-piperazine ring, the oxygen of the seven membered oxepine ring, and the tertiary bridge head nitrogen present in the 5/6 pyrrocoline ring. The infra red spectra of the alkaloid and its complexes with $VOCl_2$, $TiCl_3$ and UO_2SO_4 indicate coordination through nitrogen of acylazole group as revealed by the disappearence of CO and CN stretching vibrations in the complex. These modes occur at 1625 cm^{-1} and 1335 cm^{-1}, respectively. The position of the other bands arising from CC, CO stretching vibrations of the oxepine and those from CN stretching of the tertiary nitrogen present in the 5/6 pyrrocoline ring remains almost constant on coordination.

The information obtained from the spectra of the codeine and its complexes with Cu^{2+}, CO^{2+}, Ni^{2+}, Mn^{2+} VO^{2+}, Ti^{3+} and Cr^{3+} reveals the possibility of coordination through secondary OH group. The main evidence in favour of coordination through

OH is the absence of any band at 3600 cm^{-1} (OH stretching) or in the vicinity in the spectra of the complexes. The evidence is further supported by the non-shifting of the bands arising from NCH_3 stretching modes, and ring CC, CO stretching, ring skeletal, and CH in and out of plane vibrations of dihydrosubstituted furan ring present in the alkaloid on complexation.

Studies on the complexes of chromium(II) chloride with some amino acids

Introduction

The complexes of transition metals with amino acids are of interest[1-3] because of the biological importance of this family of compounds, and the presence of potential coordinating amino and carboxylic groups. Albert[4] has carried out a detailed study on the stability constants of various amino acid complexes, based upon pH and potentiometric measurements. He showed that the reactivities of various amino acids towards a metal ion were dependent on the stability of the resulting complexes and ionization constants. However, no attempt has been made so far to study the amino acid complexes with unstable oxidation states. The present communication reports on the composition and stabilities of chromium(II) chloride complexes of some amino acids.

Experimental

The amino acids, glycine, L-proline, DL-serine, β-alanine, DL-α-alanine, L-asparagine, L-leucine and DL-valine (B.D.H. biologically pure products) were used

and 0.01 *M* solutions were prepared in doubly-distilled, air-free water.

Chromous chloride was prepared by the method of Bathis and Bailer[5]. Chromic chloride was first reduced to chromous chloride with zinc–hydrochloric acid, and then precipitated as chromous acetate by adding ammonium acetate. The red precipitate of chromous acetate was dissolved in a minimum quantity of hydrochloric acid. The chromous chloride formed was precipitated with absolute alcohol, separated, and washed several times with small aliquots of ice-cold, air-free, doubly-distilled water. It was then dissolved in doubly-distilled water and the solution kept in an air-tight storage vessel in an atmosphere of nitrogen (pH of solution, 3.5). The solution was standardized potentiometrically by titrating with standard copper sulphate.

Carbonate-free KOH was used for preparing the aqueous solution of KOH which was stored in a Pyrex bottle fitted with a tube containing KOH for protection against atmospheric carbon dioxide. The solution was standardized by titrating with standard oxalic acid, and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out using a Tinsley potentiometer with lamp and scale arrangements using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were made with a direct reading EIL pH-meter, model 23A (England), using glass and calomel electrodes. All titrations were carried out in a specially designed cell with provision for transferring the chromous chloride solution from the storage vessel and for passing oxygen-free nitrogen in order to stir the solutions. The concentration of the chromous chloride solution was checked before the study of each system.

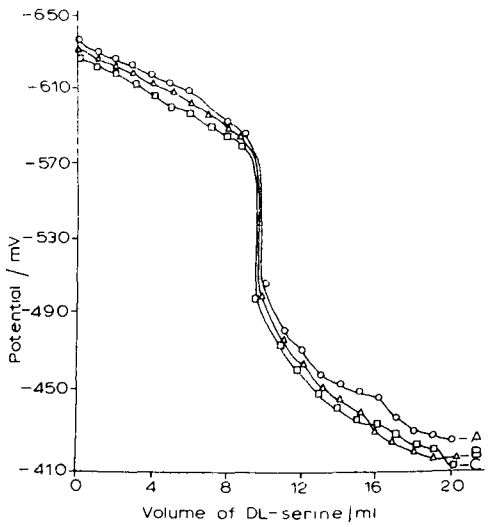


Fig. 1. Potentiometric titrations (A) 10 ml 0.666×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.666×10^{-1} *M* DL-serine (from burette), (B) 10 ml 0.50×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.50×10^{-1} *M* DL-serine (from burette), (C) 10 ml 0.44×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.44×10^{-1} *M* DL-serine (from burette).

Result and discussion

The composition of the complexes with amino acids was determined potentio-

metrically by taking various concentrations of chromous chloride (in the cell), and equimolar solutions of amino acids (from the burette) In all cases a ratio of 1 1 (chromium(II) amino acid) was obtained from the potential concentration curves (Fig 1 for DL-serine) Information concerning complex formation was obtained from pH-metric titration curves For each amino acid three sets of pH metric titrations were carried out in the order (*a*) amino acid (0 01 *M*), (*b*) chromous chloride (0 005 *M*), and (*c*) a mixture of chromous chloride and amino acid having a total concentration of 0 005 *M* and 0 01 *M* respectively using 0 1 *N* KOH as titrant The pH curves of all the amino acids show a definite shift indicating the formation of complexes of chromous chloride with amino acids (Fig 2 for DL-serine)

The complex formation constant K_c was evaluated following the method of Albert[4] The values of log K_c at $n = 1$ (where n is the average number of molecules of amino acid bound by one atom of the metal) for various amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $\bar{n}$ against $-\log [Sc]$ (Fig 3) ([Sc] is the concentration of free amino acid) By application of relation (xii) of ref 4

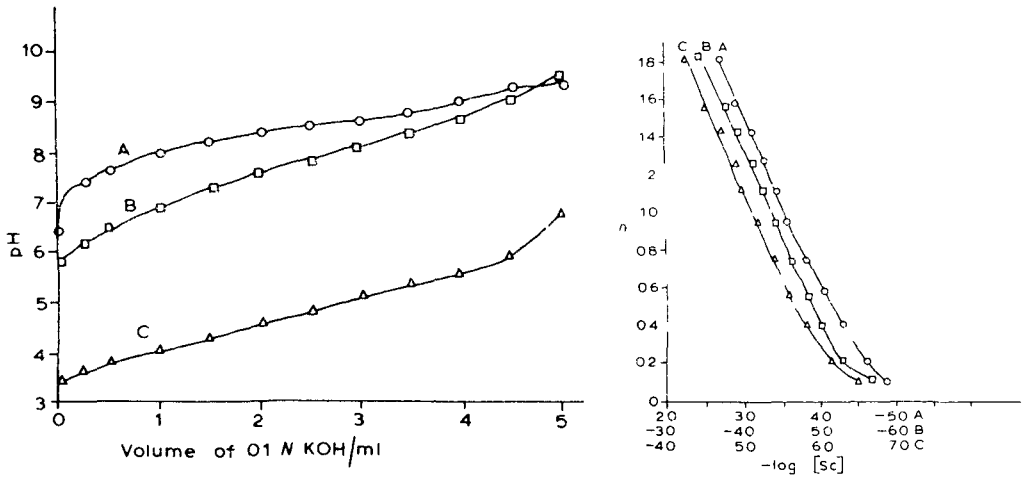


Fig 2 pH metric titrations (A) 50 ml 0 01 *M* DL serine (in cell) (B) 25 ml 0 02 *M* DL serine + 25 ml 0 01 *M* $CrCl_3$ (in cell) (C) 50 ml 0 005 *M* $CrCl_2$ (in cell)

Fig 3 Formation curves (A) DL serine chromium(II) complex (B) DL valine chromium(II) complex (C) DL proline chromium(II) complex

TABLE 1

	Graphically	*Calculated*
1 L Asparagine	6 92	6 97
2 DL α Alanine	6 72	6 76
3 β-Alanine	9 86	9 89
4 Glycine	9 02	9 05
5 DL Leucine	8 40	8 40
6 L Proline	10 32	10 35
7 DL Serine	7 20	7 21
8 DL Valine	8 70	8 68

the values of log K_s for various amino acids were evaluated. The values obtained graphically and by calculation are given in Table 1.

The values of overall stability constants obtained from the formation curve (Fig. 3) are in good agreement with those calculated.

There does not seem to be any definite correlation between the nature of the amino acid and the K_s value; however, with a few exceptions the value of K decreases with increase in chain length of carbon atoms and also seems to decrease as the distance between amino and carboxylic groups increases. These observations could not be quantitatively substantiated as no information could be obtained as to the nature of the bounding because the complexes could not be isolated. The present studies are the first to report on the chemical reaction of unstable chromium(II) ions with amino acids, and the stabilities of the resulting complexes.

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SHORT COMMUNICATIONS

Studies on the composition and stability of uranyl, vanadyl and titanous complexes with some aminoacids

A number of papers on the metal complexes of amino acids[1-4] have appeared in the literature in recent years These studies are mainly concerned with the determination of the stability constant of a complex by various electrometric methods, *viz* potentiometry, pH-metry, polarography, etc References to studies on the complexes of Cu, Zn, Fe, Ni, Co, Mn, Cd and other transition metals are available but no attempt has yet been made to investigate possible complex formation between VO^{2+}, UO_2^{2+} and Ti^{3+} ions with amino acids

The present communication deals with the behaviour of these ions towards some amino acids Formation of 1 1 complexes has been indicated by conductometric titrations, and the stability constants of the complexes have been computed from the results of pH-metric titrations

Experimental

Amino acids such as glycine, β-alanine, DL-α-alanine, L-asparagine, DL-serine, L-leucine, DL-valine and L-proline (B D H biologically pure) were used for the experiments and their solutions (0 01 *M*) were prepared in doubly-distilled water

Uranyl sulphate (B D H AnalaR), and vanadyl sulphate (B D H) were employed and solutions of these salts were analysed gravimetrically as the metal oxides[5,6] An aqueous solution of titanium(III) chloride was prepared by dissolving crystals[7] of $TiCl_3$ $6\,H_2O$ in air-free doubly-distilled water, and the solution standardized[8] Fresh solutions were always prepared before use and kept covered with a layer of kerosene oil or toluene throughout the investigations to avoid oxidation

Carbonate-free KOH solution was used for pH-metric titrations It was stored in a Pyrex bottle fitted with a KOH tube for protection against atmospheric CO_2 The solution was standardized by titrating with standard oxalic acid solution, and the strength was checked periodically before carrying out pH-metric titrations

The conductometric titrations were performed using a Philips conductivity bridge model PR 9500/90 and a dip type conductivity cell (cell constant 1 48) The pH-metric titrations were carried out with a direct reading EIL pH-meter model 23A using glass and calomel electrodes All the titrations were carried out in a specially designed cell, with provision for adding metal salt solutions from a burette, to a stirred oxygen-free system

Results and discussion

The composition of the vanadyl, uranyl and titanous complexes with various amino acids was determined conductometrically The conductometric titrations were reversible In all cases a ratio of 1 1 (metal amino acid) was established Typical curves are given in Fig 1 The pH-metric titrations were performed in triplicate for each amino acid The titrations were carried out in the order (a) amino acid (0 01 *M*),

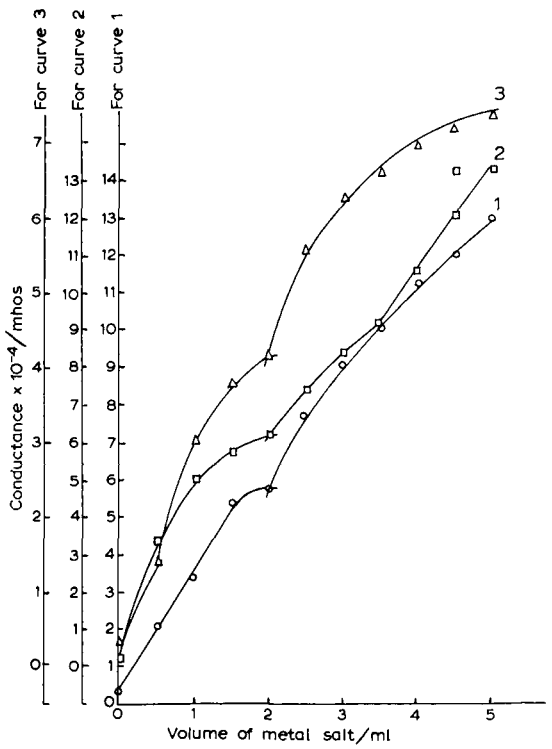

Fig 1 Reverse conductometric titrations (1) $M/15$ $TiCl_3$ added to 40 ml of $M/300$ DL-serine, (2) $M/12$ UO_2SO_4 added to 40 ml of $M/240$ DL-α-alanine, (3) $M/15$ $VOSO_4$ added to 40 ml of $M/300$ DL-valine

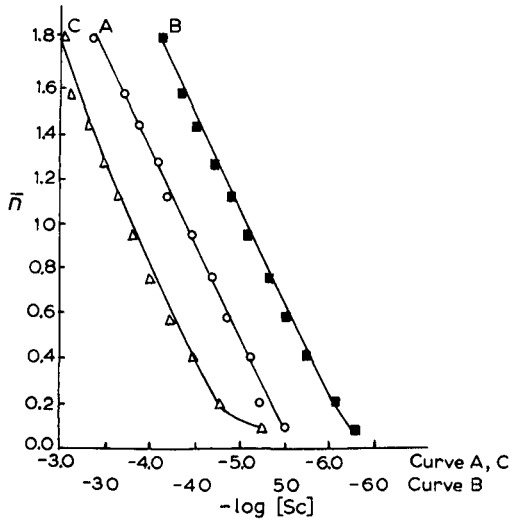

Fig 2 Formation curves (A) DL-valine–$VOSO_4$ complex, (B) DL-α-alanine–UO_2SO_4 complex, (C) DL-serine–$TiCl_3$ complex

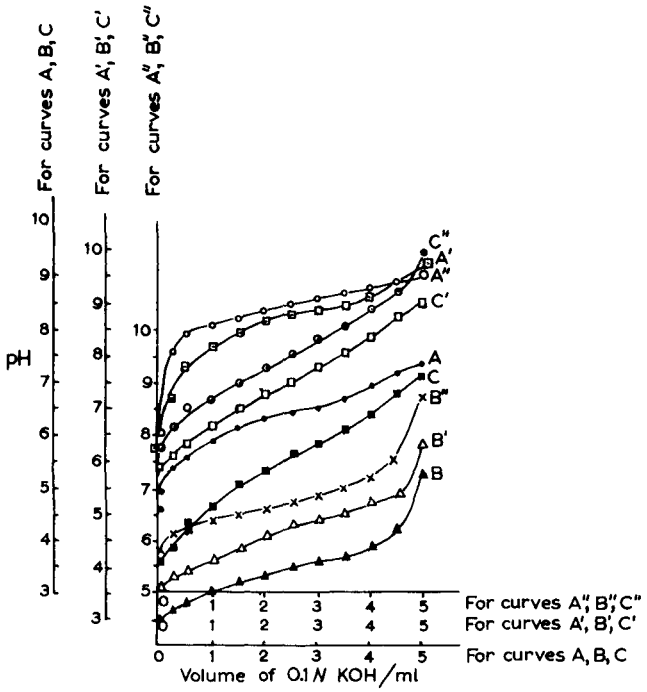

Fig 3 pH-metric titrations (A, B, C) DL-serine–$TiCl_3$, (A', B', C') DL-α-alanine–UO_2SO_4, (A', B', C') DL-valine–$VOSO_4$

TABLE 1

VALUES OF LOG (K_s/mol^2 l^{-2}) FOR VANADYL, URANYL AND TITANOUS AMINO ACIDS COMPLEXES OBTAINED BY TWO METHODS

Amino acids	*Vanadyl sulphate*		*Uranyl sulphate*		*Titanous chloride*	
	Theoretical	*Graphical*	*Theoretical*	*Graphical*	*Theoretical*	*Graphical*
L-Asparagine	6 95	6 90	6 88	6 85	7 25	7 20
β-Alanine	9 77	9 80	9 92	9 90	9 72	9 70
DL-α-Alanine	8 75	8 70	9 00	9 00	8 53	8 50
Glycine	× ×	× ×	8 62	8 65	8 52	8 50
L-Leucine	9 08	9 10	8 61	8 60	8 55	8 50
L-Proline	10 33	10 30	10 46	10 45	10 08	10 05
DL-Serine	7 54	7 50	6 86	6 90	7 60	7 60
DL-Valine	8 65	8 65	8 59	8 60	8 12	8 20

(b) metal salt (0.005 *M*) and (c) metal salt and amino acid (total concentration 0.005 *M* and 0.01 *M*, respectively), employing 0.1 *N* KOH as titrant. The pH-titration curves show appreciable shifts, indicating the formation of complexes with the amino acid (Fig. 3). The complex formation constant K_s was evaluated by the method modified by Albert[4].

The values of log K_s at $\bar{n}=1$, where $\bar{n}$ is the average number of molecules of

amino acid bound by one atom of the metal ion, were calculated from the values of $-\log$ [Sc] obtained by plotting $\bar{n}$ *vs.* $-\log$ [Sc] (Fig. 2). [Sc] is the concentration of the free amino acid. The values of log K_s for various amino acids evaluated from the formation curves, and those calculated are given in Table 1.

The values of the overall stability constants log K_s obtained from the formation curves (Fig. 2), are in good agreement with those calculated.

Uranyl sulphate, vanadyl sulphate and titanous chloride form 1 : 1 complexes with various amino acids (L-asparagine, β-alanine, DL-α-alanine, glycine, L-leucine, L-proline, L-serine and DL-valine). In the vanadyl and titanous complexes the values of log K_s vary from L-asparagine (6.95, 7.25) to L-proline (10.33, 10.08), whereas in uranyl complexes the variation is from DL-serine (6.86) to L-proline (10.46). There does not seem to be any correlation between the nature of the aminoacids and the K_s values although, with a few exceptions, the latter decreases with increase in chain length of carbon atoms. The real nature of bonding in these complexes is a matter of speculation as no complex could be isolated in a sufficiently pure form.

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Complexes of chromium(II) chloride with some sulphur-containing amino acids

The interaction of transition metal ions with amino acids covers a vast area of research because of its biological importance, and the coordinating ability of amino and carboxylic groups[1-3]. However, very few papers deal with the interaction of amino acids with transition metals having abnormal oxidation states. Recently a systematic study on this aspect of the problem was undertaken by the authors and the complexes of Cr^{2+}, UO_2^{2+}, VO^{2+} and Ti^{3+} with non-sulphur containing amino acids were studied[4,5]. The present communication deals with the composition of various sulphur-containing amino acid complexes, based upon pH-metric and potentiometric measurements.

Experimental

The amino acids, DL-methionine, taurine and cysteine (B.D.H. Biologically pure products) were used and 0.01 *M* solutions were prepared in doubly distilled air-free water. Chromous chloride was prepared by the method of Bathis and Bailer[6]. The aqueous solution of chromous chloride was prepared as described previously, and stored in an air-tight storage vessel under an atmosphere of oxygen-free nitrogen (pH 3.5). The solution was standardized potentiometrically by titration with standard copper sulphate. Carbonate-free KOH was used to prepare an aqueous solution of KOH and the solution was kept in a Pyrex bottle fitted with a guard tube containing KOH for protection against atmospheric carbon dioxide. The solution was standard-

ized by titrating with standard oxalic acid and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out with a Tinsley potentiometer having a lamp and scale arrangement and employing platinum and calomel electrodes. The pH-metric titrations were performed with a direct reading EIL pH-meter model 23A (England). All the titrations were carried out in a specially designed cell described previously. The concentration of chromous chloride was checked before studying each system. All investigations were carried out at 25°C.

Results and discussion

Chromous chloride forms 1:1 complexes with DL-methionine, taurine and cysteine as determined from potentiometric curves (Fig. 1). The titrations were carried out using various concentrations of chromous chloride in the cell and equimolar solution of amino acids. The information regarding complex formation was obtained by noting the shifts in the pH-titration curves.

For each amino acid three sets of pH-metric titrations using 0.1 *N* KOH as a titrant were carried out in the order: (a) amino acid 0.01 *M*, (b) chromous chloride 0.005 *M* and (c) a mixture of chromous chloride and amino acid having a total concentration of 0.005 *M* and 0.01 *M*, respectively, (Fig. 2).

The values of the logarithm of the formation constant, log K_s at $\bar{n}=1$ (where $\bar{n}$ is the average number of molecules of amino acid bound by one atom of the metal) for the amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $\bar{n}$ *vs.* $-\log [Sc]$, where $[Sc]$ is the concentration of free amino acid (Fig. 3). By applying the relation $\log K_s = -2 \log [Sc]$, values of the formation constants for all three amino acids were evaluated[7]. The values obtained graphically and by calculation

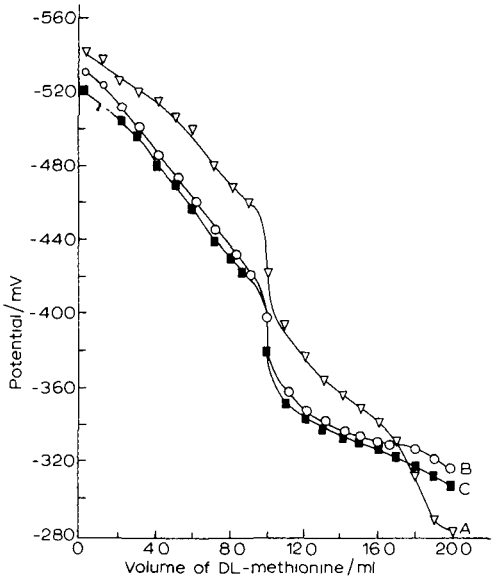
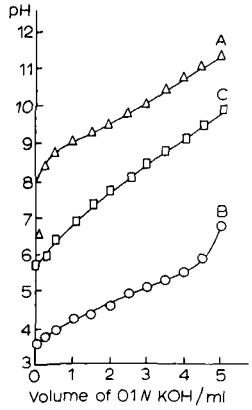


Fig 1 Potentiometric titrations (A) 10 ml 0.666×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.666×10^{-1} *M* DL-methionine (from burette), (B) 10 ml 0.50×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.50×10^{-1} *M* DL-methionine (from burette), (C) 10 ml 0.44×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.44×10^{-1} *M* DL-methionine (from burette)



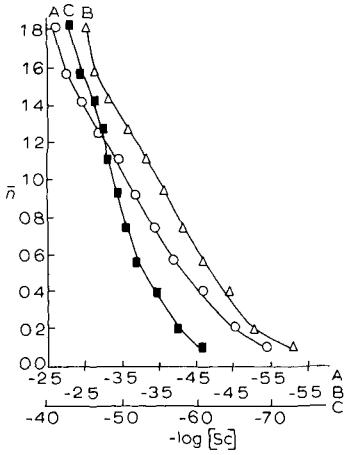


Fig 2 pH-metric titrations (A) 50 ml 0.01 *M* DL-methionine (in cell), (B) 50 ml 0.005 *M* $CrCl_2$ (in cell), (C) 25 ml 0.02 *M* DL-methionine + 25 ml of 0.01 *M* $CrCl_2$ (in cell)

Fig 3 Formation curves (A) DL-methionine–chromium(II) complex, (B) taurine–chromium(II) complex, (C) cysteine–chromium(II) complex

are given in Table 1.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. The values of log K_s given in Table 1

TABLE 1

		log (K_s/mol^2 l^{-2})	
		Graphically	*Calcd*
1	Cysteine–chromium(II) chloride complex	9.80	9.77
2	DL-Methionine–chromium(II) chloride complex	7.32	7.30
3	Taurine–chromium(II) chloride complex	7.02	7.06

give an indication of the possible correlation between the nature of the amino acids and overall stability constants. The value of log K_s decreases as the distance between amino and carboxylic group increases (between NH_2 and $-SO_2OH$ in the case of taurine). The present studies do not clarify the part played by sulphur atoms.

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